IMPERIAL AGRICULTURAL
RESEARCH INSTITUTE, NEW DELHI.

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THE ANNALS

AND

MAGAZINE OF NATURAL HISTORY.

[TENTH SERIES.]

> "……………… per litora spargite muscum
> Naiades, et circùm vitreos considite fontes:
> Pollice virgineo teneros hic carpite flores:
> Floribus et pictum, divæ, replete canistrum.
> At vos, o Nymphæ Craterides, ite sub undas
> Ite, recurvato variata corallia trunco
> Vellite muscosis e rupibus, et mihi conchas
> Ferte, Deæ pelagi, et pingui conchylia succo."
> *N. Parthenii Giannettasi*, Ecl. 1.

No. 25. JANUARY 1930.

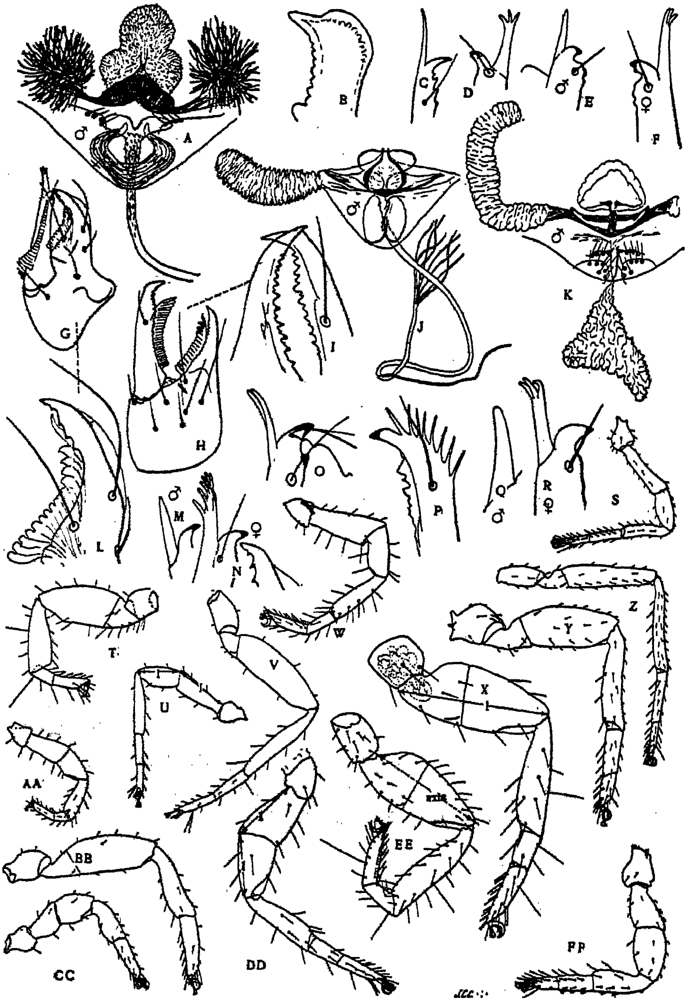
I.—*A Synoptic Classification of the False Scorpions or Chela-spinners, with a Report on a Cosmopolitan Collection of the same.*—Part II. *The Diplosphyronida* (*Arachnida-Chelonethida*). By JOSEPH CONRAD CHAMBERLIN, A.B., M.A., Stanford University, California, U.S.A.

1. INTRODUCTION.

As in the first paper of this series (Chamberlin, 1929), a number of figures (figs. 1–3) are herewith given in order to elucidate the terminology employed and to illustrate the more important systematic distinctions. They are not primarily designed to illustrate particular species; hence the form of the captions and the nature of the citations.

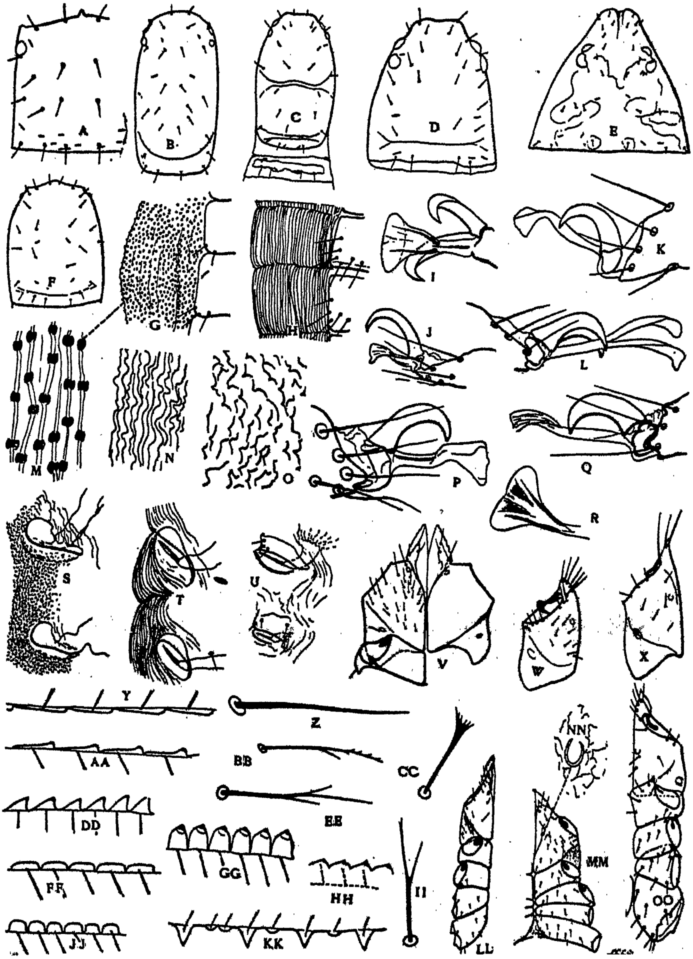
In the Diplosphyronids palpal proportions, within certain limits, are of primary importance, especially in discriminating between species. It is therefore of importance that measurements be taken in a standardized way from definite key-points. All palpal measurements must be taken as illustrated in fig. 3 X in order to yield results strictly comparable with those given in this paper. The term femur-patella which is occasionally employed in connection with

Fig. 1.



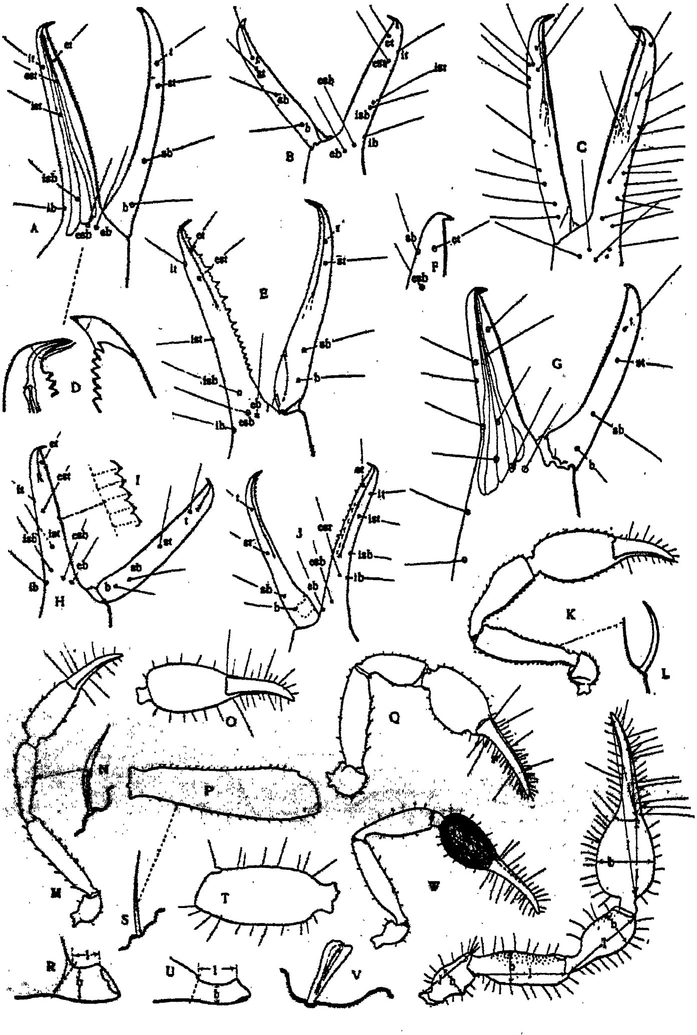
Structures of systematic significance in the Diplosphyronida. Characteristic types of male genitalia, A, J, K. Spinnerets, B, C, D, E, F, M, N, O, P, Q, R. Sexual differentation in galeate spinnerets, E, F; M, N; Q, R. Serridentate chelicera, H, I. Unilobate chelicera, G, L. Subapical lobe of unilobate chelicera, E, F, O, R. Morphological variation in leg iv., T, V, X, Y, Z, BB, EE. Morphological variation in leg i., S, U, W, AA, CC, DD, FF.

Fig. 2.



Structures of systematic significance in the Diplosphyronida. Carapacal types, A, B, C, D, E, F. Pleural membrane types, G, H. M, N, O. Empodia, I, J, K, L, P, Q, R. Spiracles, S, T, U. Maxillæ, V, W, X. Marginal teeth of chelæ (orientation, apex of fingers to left), Y, AA, DD, FF, GG, HH, JJ, KK. Subterminal setæ of tarsus, Z, BB, CC, EE, II. Coxæ, LL, MM, OO.

Fig. 3.



Structures of systematic significance in the Diplosphyronida. Chelæ showing dentition, chætotaxy, and venom-system, A, B, C, D, E, F, G, H, I, J. Various diplosphyronid palpi, K, M, Q, W, X. Palp showing mode of taking measurements, X. Tibial pedicels showing mode of taking length and breadth, R, U. Details of palpal structures, L, N, O, P, S, T, V.

leg iv. comprises both those segments taken as a unit, and is to be measured as indicated in fig. 1 X. The length so taken is not to be considered as taken along the longitudinal axis of the compound segment. This latter, as here understood, is indicated in fig. 1 EE. The relative lengths of femur and patella of leg i. are occasionally of systematic importance. Their lengths should be measured as indicated in figs. 1 U & DD. The slenderness of the pedicel of the tibial segment of the palpus is of importance in certain groups. Its length and breadth is to be taken as indicated in figs. 3 R & U.

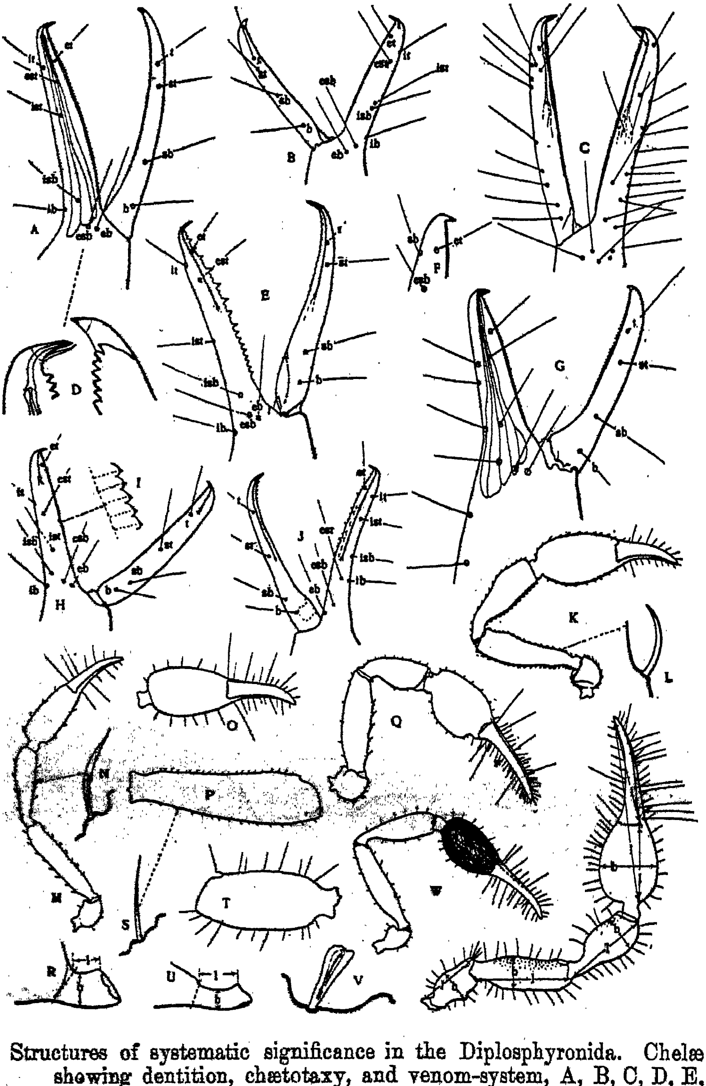
Ordinarily variation in proportions is small. At the same time it must be recognized that where material is scanty (as is all too frequently the case) it is not possible to say whether the particular proportions stated are typical (average) or extreme. Hence considerable allowance must be made for this factor in practical work, especially in the case of species known from but one or two specimens each. In this connection it is important to keep in mind the general fact that the female, in nearly every case, is significantly larger and stouter in its proportions than the male. In my experience I know of only a few cases where the length of a palpal segment, for instance, will vary in its extremes more than 0·5–0·8 its own breadth. Where more than one specimen is available for study the extremes of proportion actually observed are given, and these are not sexually differentiated unless the variation due to this factor is considerable, or unless there is a tendency toward "overlapping" on the part of it and a closely related form. Where a series of proportions are derived from a single specimen the actually observed proportions are given, and no range of variation is indicated except rarely in keys, where this may be estimated within reasonable limits on the basis of other criteria.

The descriptive term *subequal* as employed herein in comparing relative lengths of parts means merely that the two contrasted structures are essentially equal within very small limits of variation in either direction.

Total body-length as an index of size is frequently useful. This measurement is taken from the anterior carapacal margin to the tip of the abdomen, and is from specimens which have been treated in caustic potash and mounted in Canada balsam. Alcoholic material will ordinarily measure distinctly less, about in the ratio of 9 to 10 ordinarily.

The chætotaxy of the chela is of great systematic importance. Various typical arrangements of tactile setæ

Fig. 3.



Structures of systematic significance in the Diplosphyronida. Chelæ showing dentition, chætotaxy, and venom-system, A, B, C, D, E, F, G, H, I, J. Various diplosphyronid palpi, K, M, Q, W, X. Palp showing mode of taking measurements, X. Tibial pedicels showing mode of taking length and breadth, R, U. Details of palpal structures, L, N, O, P, S, T, V.

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Total body-length as an index of size is frequently useful. This measurement is taken from the anterior carapacal margin to the tip of the abdomen, and is from specimens which have been treated in caustic potash and mounted in Canada balsam. Alcoholic material will ordinarily measure distinctly less, about in the ratio of 9 to 10 ordinarily.

The chætotaxy of the chela is of great systematic importance. Various typical arrangements of tactile setæ clearly illustrating the terminology employed in their connection are illustrated in figs. 3 A, B, C, E, H, J, and G. The tactile setæ are referred to individually throughout this work by the abbreviations indicated in the figures, with the exception that in the text they are always cited in capitals, thus: ET, EST, IT, etc. Their position is often indicated in terms of finger-lengths or, rather, fractions thereof. In such cases a finger-length (whether referring to fixed or movable finger) is the length of the movable finger as seen from a lateral aspect and taken from its apical tooth to its proximal exterior angle. When close together the distance between tactile setæ may be stated in terms of areolar diameters. An areolar diameter is to be understood as the diameter of the areole of one of the tactile setæ of the chela. It is a useful and reliable unit of measurement.

The nature of the venom-apparatus is of primary systematic importance, and must be ascertained with care. This can easily be done from a chela which has been dissected off, opened up, carefully cleared, and mounted on its side in Canada balsam. All the gross structures of the venom-apparatus may then be seen through the translucent chitin. Two of the possible three variants in the distribution of the venom-apparatus are found in this suborder—*i. e.*, it may be present in both fixed and movable finger (figs. 3 C, E, H, & J); or it may occur only in the fixed finger (figs. 3 A, B, D, & G).

In some groups the carapacal chætotaxy is stated as a formula (*e. g.*, 4–6 (24)). Interpreted, this particular formula indicates that the anterior margin is bordered by 4, the posterior margin by 6, while the carapace as a whole bears a total of 24 setæ.

2. SYSTEMATIC SECTION.

Section HOMOSPHYRONIDA, J. C. Chamberlin.

1929. J. C. Chamberlin, p. 78 *.

Suborder DIPLOSPHYRONIDA, J. C. Chamberlin.

1929. J. C. Chamberlin, p. 78.

Type. The family Garypidæ, Hansen.

Remarks. Cosmopolitan in distribution. Includes seven families and two superfamilies, which are characterized in the following key:—

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* These references are to the "Bibliography," which will appear at the end of the paper.

Analytical Key to the Superfamilies and Families of the Diplosphyronida.

1. Both fore and hind legs comprising but a single tarsal segment (fig. 1 BB, CC) .. 8.

Both fore and hind legs comprising two tarsal segments each (fig. 1 T, AA; U, V; W, EE) .... 2.

2. Movable finger of chelicera clearly multidenticulate, without a true subapical lobe (fig. 1 H, I, C, P); serrula interior truly serrulate throughout and not basally laminate (fig. 1 H); subterminal seta, with few exceptions, forked or otherwise toothed or modified (fig. 2 BB, CC, EE, II); carapace generally epistomally produced (fig. 2 A, F). (Superfamily NEOBISIOIDEA, nov.) .... 3.

Movable finger of chelicera with a single (rarely secondarily subdivided (fig. 1 F, F)) subapical lobe or tooth, never multidenticulate (fig. 1 G, D, O, R); teeth of serrula interior basally fused (proximally at least) to form a membranous plate, apical teeth strongly differentiated and non-serrulate (fig. 1 L); subterminal setæ in all known cases completely simple and acute (fig. 2 Z); carapace often somewhat emarginate and rarely if ever epistomally produced (fig. 2 B, C, D, E). (Superfamily GARYPOIDEA, nov.) .... 6.

3. Venom-apparatus developed in fixed finger only, the tip of the movable finger with a definite sheath differentiated for the reception of the venedens (fig. 3 A, B, D). 4.

Venom-apparatus developed in both fixed and movable fingers, a definite sheathing device only rarely being developed on either finger (fig. 3 C, E, H, J) .... 5.

4. Pleural membrane of abdomen smoothly longitudinally plicate, never granulate (fig. 2 H); femoral articulation of leg iv. at least slightly oblique to *longitudinal axis* (fig. 1 X), and generally strongly so (almost as in fig. 1 T) .... Family SYARINIDÆ, nov., p. 38.

Pleural membrane of abdomen granulate or granulo-striate (fig. 2 G, M); femoral articulation of leg iv. truly vertical to long axis of femur-patella (fig. 1 EE) .. Family NEOBISIIDÆ, nom. nov., p. 9.

5. Pleural membrane of abdomen granulate (fig. 2 G); with the normal complement of 12 tactile setæ on fingers of chela (fig. 3 J); subterminal seta in only known case simple and acute (fig. 2 Z) .... Family HYIDÆ, nov., p. 41.

Pleural membrane of abdomen evenly longitudinally plicate (fig. 2 H); usually (except in *Bochica*) with many tactile setæ on fingers of chela, far in excess of the normal 12 (fig. 3 C); subterminal seta in all known cases more or less dentate or forked (about as in figs. 2 BB, EE, II). Family IDEORONCIDÆ, [nov., p. 42

6. Venom-apparatus developed in fixed finger only, a well-marked sheathing device developed on opposing movable finger (fig. 3 G, D); fixed finger of chela with more than the normal complement of 8 tactile setæ (11–12) in all known cases (fig. 3 G); pleural membrane smoothly plicate; carapace extremely sclerotic and very elongate (fig. 2 B) .... Family MENTHIDÆ, [nov.

Venom-apparatus developed in both fixed and movable finger, no sheathing device developed on either finger (fig. 3 H, J); chela with the normal 12 tactile setæ at most (fig. 3 H, J); pleural membrane plicate or wrinkled; carapace variously modified, but not as above (fig. 2 C, D, E). 7.

7. Pleural membrane smoothly and evenly plicate (fig. 2 H); carapace only rarely significantly triangular (fig. 2 C, D); abdomen not subovate, but with more or less parallel sides, not greatly broader than cephalothorax; vestitural setæ of palpal femur and tibia prominent (or relatively so) and always slenderly acute (fig. 3 T); stigmatic helix small, but always clearly present (fig. 2 T) .... Family OLPIIDÆ, nov.

Pleural membrane granulo-hispid or wrinkled-plicate (fig. 2 S, O, N); carapace always significantly triangular (fig. 2 E); abdomen always subovate and much broader than cephalothorax; vestitural setæ of palpal femur and tibia markedly short and inconspicuous, the shortness being especially noticeable if the setæ are acute (fig. 3 P, S; also M, N, Q, K, L, V); stigmatic helix present or absent (fig. 2 S, U) .... Family GARYPIDÆ, [Hansen.

8. With four well-developed eyes .... 9.

With two or no eyes .... Family CHELIFERIDÆ, [Hansen (old sense) *.

9. Carapace typically garypoid (fig. 2 E); abdomen without pleural plates and carapace, with neither alæ nor horn-like protuberances anterior to the eyes; legs i. and iv. strongly differentiated morphologically (fig. 1 BB, CC) .... Genus *Synsphyronus*, [nov., of the family Garypidæ.

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* Not treated herein. This "family," or, rather, complex of families, will include the bulk of the forms to be treated in Part III. of the present series of papers.

Carapace not garypoid, with at least two prominent horn-like protuberances anterior to the eyes; with either carapacal alæ or abdominal pleural plates; legs i. and iv. of essentially the same morphological structure	Family FEÆLLIDÆ, [Ellingsen *.

Superfamily *NEOBISIOIDEA*, nov.

Type. Family Neobisiidæ, nom. nov.

Diagnosis and Remarks. Characterized in preceding key. Cosmopolitan in distribution, but, so far as present knowledge is concerned, predominantly of the Northern Hemisphere.

Family **Neobisiidæ**, nom. nov.

1894. *Obisiidæ*, Hansen, p. 231.
1906. *Obisiidæ*, With, p. 74.

Type. The genus *Neobisium*, nom. nov.

Diagnosis and Remarks. Characterized in key to families. Cosmopolitan in distribution, but predominantly Holarctic. Includes two well-marked subfamilies, which are diagnosed in the following couplet:—

Key to the Subfamilies of the Neobisiidæ.

Spinneret present or absent; if present, never galeate, but represented at most by a strongly sclerotic knob (fig. 1 B, I)	NEOBISIINÆ, p. 9.
Spinneret always present as one or more transparent galeal processes (fig. 1 C, D, P)	IDEOBISIINÆ, p. 22.

Subfamily *NEOBISIINÆ*, **nom. nov.**

1879. *Obisiinæ*, Simon, vii. p. 50.
1894. *Obisiinæ*, Hansen, p. 232.
1906. *Obisiinæ*, With, p. 75.
1928. *Obisiinæ*, Kästner, p. 9.

Type. The genus *Neobisium*, nom. nov.

Diagnosis and Remarks. Characterized in key. The substitution of the name Neobisiinæ for Obisiinæ is elucidated under the generic heading. All members of this subfamily are apparently Holarctic in distribution. The included genera and subgenera are characterized in the following analytical key :—

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* Not dealt with in this paper. See Chamberlin, 1923 (*a*).

Key to the Genera and Subgenera of the Neobisiinæ.

1. SB and ISB absent (*i. e.*, 3 tactile setæ on movable and 7 on fixed fingers of chela); T and ST 3–5 areolar diameters apart; apical curve of maxilla with 3 border-setæ . *Microbisium*, p. 20.

T and ISB present (*i. e.*, 4 tactile setæ on movable and 8 on fixed fingers of chela); ST and SB at least 6 or 7 areolar diameters apart, SB clearly closer to B than to ST; apical curve of maxilla with 4 or 5 border-setæ (fig. 2 W) .... 2.

2. ET, EST, and IT clearly situated on distal fourth, or more usually fifth, of fixed finger; legs and palp extraordinarily slender—fingers of palps four or more times as long as breadth of chela; blind European cave-dwelling species .... *Blothrus*, p. 11.

ET, EST, and IT not all included on distal fourth or fifth of fixed finger (generally on distal third (fig. 3 A); legs and palpi not unusually slender—fingers of chela rarely (and then but little) more than twice as long as breadth of chela; non-cave forms generally with either two or four eyes (if eyes, as is rarely the case, are extremely reduced or possibly absent, separation is easily effected on the basis of preceding characters). (Genus *Neobisium*, nom. nov.) .... 3.

3. IST clearly on basal half of fixed finger of chela, forming together with EB, ESB, IB, and ISB a subbasal group of five tactile setæ; EST clearly submedian, and about as close to ISB as to ET; femur no longer than carapace (eyes four; in one species these are very weakly developed, and blind species may be expected) .... Subgenus *Parobisium*, [p. 17.

IST at least submedian and generally anterior of median; an isolated basal cluster of five setæ never developed; femur of palpus always clearly longer than carapace (eyes two or four) .... 4.

4. With two eyes; IST and ISB more or less median between the two groups of ET, EST, IT, and EB, ESB, and IB respectively, so that these two clusters of setæ are more or less connected by IST and ISB as intermediates .... Subgenus *Roncus*, [p. 12.

With four eyes; IST closely associated with EST, ET, and IT, while ISB is closely associated with the basal group of setæ, so that nearly half a finger-length of vacant space intervenes between these two groups of four tactile setæ each (fig. 3 A) ...... Subgenus *Neobisium*, [p. 13.

Genus BLOTHRUS, Schiϕdte.

1848. *Blothrus,* Schiϕdte, p. 23.

Genotype. *Blothrus spelæus,* Schiϕdte.

Remarks. As re-characterized this genus comprises a compact and apparently natural group of European cave-species. In addition to the two species specifically referred to below, the following forms almost certainly pertain to this genus as here defined :—*Obisium* (*Blothrus*) *jeannelli,* Ellingsen, from Spain; *Obisium* (*Blothrus*) *bolivari,* Nonidez, from Spain; *Obisium* (*Blothrus*) *cerberus,* Simon, from France; *Obisium* (*Blothrus*) *antrorum,* Simon, from France; *Obisium* (*Blothrus*) *torrei,* Simon, from Italy; *Obisium* (*Blothrus*) *peyerimhoffi,* Simon, from "Basses-Alpes"; *Obisium* (*Blothrus*) *breuili,* Bolivar & Pieltain, from Spain; and *Obisium* (*Blothrus*) *nonidezi,* Bolivar & Pieltain, from Spain.

"*Blothrus*" *magnus,* Ewing, and "*Blothrus*" *californicus,* Banks, do not in any wise pertain to this genus.

Blothrus spelæus, Schiϕdte.

1848. *Blothrus spelæus,* Schiϕdte, p. 23, figs.

Material examined. ♀, co-type (JC. 407.01001), loaned through the courtesy of Dr. Kai L. Henriksen. 1 ♀ (JC. 35.01001), Carniole Grotto, France; exchange from Dr. Louis Fage. The type-collection was from Adelsburg Cave.

Remarks. The French specimen, while pallid, was less so than Schiϕdte's co-type.

Blothrus abeilli, Simon.

1872. *Blothrus abeilli,* Simon, p. 224, figs.

Material examined. 1 ♀ (JC. 34.01001), from the Grotto de St. Guilhern, Herault, France. Exchange from Dr. Louis Fage.

Remarks. A more robust and less pallid species than *spelæus.*

Genus NEOBISIUM, nom. nov.

1817. *Obisium,* Leach (in part.), pp. 48–53.
1879. *Obisium,* Simon, p. 51.
1906. *Obisium,* With, p. 76.
1911. *Obisium,* Kew, p. 54.
1928. *Obisium,* Kästner, p. 10.

Genotype. *Obisium muscorum,* Leach. Designated by Simon.

Historical Identity. The genus *Obisium* was proposed by Illiger in 1798, with *Chelifer cancroides* (Linn.) as its only included species. As pointed out by Kew in 1911 (p. 54, footnote 2) this makes it a strict synonym of *Chelifer*, Geoffroy. The adoption of the name by Leach for use in connection with the species *muscorum* cannot be sustained. A new name therefore becomes necessary for the present group, which, in spite of the very evident synonymy, has gone under the name of *Obisium* ever since Leach's time. *Neobisium* is therefore proposed as a substitute. The change is regrettable, but impossible to avoid under the International Rules of Nomenclature.

Diagnosis and Remarks. Characterized in key. This is primarily a Palæarctic genus, reaching its greatest development in Europe. It has one or two eastern North American representatives. Most, if not all, of European false scorpions previously assigned to the genus *Obisium*, sensu stricto, belong here. This is probably not the case with *most* extra-European forms.

Subgenus Roncus, L. Koch.

1873. *Roncus*, L. Koch, p. 44.
1879. *Roncus*, E. Simon, p. 63.
1911. *Roncus*, Kew, p. 53.

Genotype. *Roncus lubricus*, L. Koch.

Diagnosis and Remarks. Characterized in preceding key. Two species were originally ascribed to the genus *Roncus* by Koch. One of these, *Roncus cambridgei*, is not a true *Neobisium*, but rather a member of the genus *Microcreagris*. The only species certainly referable to the subgenus are strictly European.

Neobisium (*Roncus*) *lubricus*, L. Koch.

1873. *Roncus lubricus*, L. Koch, p. 44.
1911. *Obisium* (*Roncus*) *lubricum*, L. Koch, Kew, p. 53.
1928. *Roncus lubricus*, L. Koch, Kästner, p. 10.

Material examined. 1 ♀ (JC. 27.01001), from Bona Algiers, exchange from M. Louis Fage. 1 ♀ (JC. 31.01001), from Genoa, Italy (Ellingsen's determination); exchange from British Museum.

Neobisium (*Roncus*) *abditus*, sp. n.

(Figs. 1 H, I, W, EE; figs. 2 II, OO; fig. 3 X.)

Holotype, ♂ (JC. 511.05001); allotype, ♀ (JC. 511. 05003). Paratopotypes: ♂, ♀, and ⊙ (JC. 511.05002, 511.05004–17, and 511.06001). All from Sorgono, Sardinia, where they were collected by Dr. Anton Krausse; labelled "13.4.1.2.30." All but specimens 511.05004 to 7 (2 ♂ and 2 ♀) are in collections of British Museum of Natural History; latter in author's collection.

Diagnosis. Both fixed and movable fingers, bearing 46–48 well-developed marginal teeth. Carapace subquadrate; two weakly developed eyes, which are more than a diameter from the anterior carapacal margin. Tergites with 11 or 12 and sternites with 12 or 13 marginal setæ. Palpus (fig. 3 X) robust, femur clearly granulate along its anterior face. Trochanter 2·2 to 2·3 times as long as broad; femur 2·9 to 3·1 times as long as broad, shorter than length of carapace; tibia strongly pedicellate, the pedicel measuring nearly a fourth of the total length of the segment, 2·1 to 2·3 times as long as broad; chela 2·8 to 3·1 times as long as broad; fingers slightly longer than hand. Length about 2·0 mm.

Remarks. It is possible that *abditus* represents an already described species, but this cannot be ascertained on the basis of the extant literature. The general systematic principle, that a synonym is a lesser taxonomic sin than a misdetermination, has been followed.

Subgenus Neobisium, typicus.

Genotype. *Obisium muscorum*, Leach.

Diagnosis and Remarks. Characterized in preceding key. Species clearly pertaining to this group as here defined are known from nearly the whole of Europe and middle eastern United States. A comprehensive and thorough revision of European, particularly southern European, species is badly needed.

Neobisium muscorum (Leach).

1817. *Obisium muscorum*, Leach, p. 51.
1911. *Obisium muscorum*, Leach, Kew, p. 54.
1928. *Obisium muscorum*, Leach, Kästner, p. 11.

Types. Deposited in the British Museum of Natural History, where they have been studied both by Cambridge and Kew.

Material examined. 2 ♀ (JC. 26.01001–2), Skăue, Skäralio, Sweden; exchange A. Tullgren. 1 ♀ (JC. 25.01001), Denmark; exchange Dr. Kai L. Henriksen. 1 ♀ (JC. 24.01001), Glogan, England; exchange British Museum. 1 ♂ (JC. 23.01002), "France"; exchange Dr. Louis Fage.

3 ♂, 3 ♀ (JC. 326.01001, "Bürgst bÿ Breda"; JC. 327.01001, "Hilversum"; JC. 328.01001, "Aauspoelsel raeburg"; JC. 329.01001–3, "Diener"), Holland, from decaying leaves; examined through the courtesy of Dr. A. C. Oudemans.

Neobisium incertum, sp. n. (Fig. 1 K; fig. 2 EE.)

Holotype, ♂ (JC. 511.07001); allotype, ♀ (JC. 511.07004); paratopotypes, ♂ and ♀ (JC. 511.06002–3 and 511.07005 to 15). Sorgono, Sardinia. Coll. Dr. Anton Krausse. Property of British Museum of Natural History, except paratypes, JC. 511.07005–9 (2 ♂ and 3 ♀), which are in the author's collection. Sixteen immature specimens (JC. 511.09001–16) collected at the same time and place are probably members of this species. Orginally misdetermined by myself (and so labelled in the case of the British Museum material) as *Obisium muscorum*, Leach.

Diagnosis. Fingers of chela subequal in length; marginal teeth normal on fixed finger, much reduced or obsolete on basal two-thirds of movable finger, contiguous and uniform in size. Carapace typical; espistomal process prominent. Palps robust and completely non-granulate. Trochanter normal; femur with a few scattered rounded protuberances, but otherwise smooth and polished, gradually swollen from base, attaining its greatest diameter ⅓ its length from the tip, 3·6–4·0 times as long as broad; tibia very convex on inner margin, about 2·2 times as long as broad; chela 3·5 to 3·6 times as long as broad; fingers much longer than hand and shorter than femur, which is in turn shorter than the carapace. Length 2·6–3·0 mm.

Remarks. Closely similar in many ways to *Neobisium erythrodactylum* (L. Koch). The tibia, however, is very much more convex on the inner margin, and the chela is unicolorous.

Neobisium inæqualum, sp. n.

Holotype, ♂ (JC. 13.01010); allotype, ♀ (JC. 13.01002); paratopotypes, 3 ♂ and 5 ♀ (JC. 13.01001 and 13.01003–9 and 11–12). All from "Hungary orientalis," Europe. Received from Dr. Chas. Sajo of Oersentmiklos.

Diagnosis. Fingers of chela clearly unequal in length, the movable finger being distinctly the longer; marginal teeth best developed on fixed finger, low and poorly developed on basal ¾ of movable finger, subcontiguous and of uniform size (*i. e.*, large teeth not alternating with several smaller ones). Carapace typical; epistomal process well defined, anterior eyes ½ diameter from anterior margin of carapace and ⅕ diameter from posterior pair. Palps robust, tibia and chela prominently pedicellate; non-granulate. Trochanter with rounded tubercle behind; femur not pedicellate, gradually enlarging in diameter to near its tip, about 1·5 times as long as carapace and 4·3 to 4·6 times as long as broad; tibial pedicel much longer than broad; tibia exteriorly slightly convex, interior strongly swollen medianally, with a slight concavity distally, 2·5 to 2·7 times as long as broad; chela unusually broad at base of fingers, so that latter appear to arise from a subtruncate base; pedicel as long as broad; hand egg-shaped and subequally expanded interiorly and exteriorly, 3·6 to 3·7 times as broad as long (length taken to tip of *fixed* finger); fingers clearly longer than hand, movable finger much longer than fixed finger. Tergites with about 14, sternites with about 20, marginal setæ. Length about 3·0 mm.

Remarks. Apparently related to *Neobisium elimatum* (C. Koch), which it resembles in the unequal fingers of the chela. It seems to differ therefrom in larger size, more pedicellate chela and tibia, and in the broader carapace.

Neobisium sp. indet.

Material examined. 1 ♂ (JC. 23.01001); France, exchange from M. Louis Fage.

Remarks. This species when received was erroneously determined as *muscorum* (Leach), probably by Simon. It may be *carpenteri* (Kew) or *simile* (L. Koch). Kew (1911, p. 54, footnote 2) has already shown that Simon had confused these three forms. The specimen before me is in too poor condition to permit a definite conclusion.

Neobisium carolinensis (Banks).
(Figs. 2 G, M, W; figs. 3 A, D.)

1895. *Obisium carolinensis*, Banks, p. 12.

Material examined. North Carolina: Frying Pan Gap, Mt. Pisgáh ‡, 1 (JC. 317.01001). Mt. Pisgáh ‡, 10.14.1926, 5 (JC. 315.01001–5). Headwaters, East Fork of Pisgáh River ‡, 10.14 1926, 1 (JC. 319.01001). Grandfather Mountain †, 10.12.1923, 13 (JC. 302.01001–13). Summit of Mt. Mitchell †, 10.22.1923, 25 (JC. 318.02001–25). Blowing Rock †, 10.10.1923, 3 (JC. 303.01001–3). Black Mountains †, 5 (JC. 14.01001–5), coll. R. V. Chamberlin. Montreat*, 10.16.1923, 11 (JC. 316.01001–11). Mt. Pisgáh ‡, Oct. 1923, 10 (JC. 304.01001–10). Nantahala Gap ‡, Macon.

dagger (‡) are probably more similar to *tenuis* than to the typical variety, but apparently represent true intergrades. Much further study will be required before the real status of this "species" can be ascertained.

Neobisium (?) sp. indet.

Material examined. 8, apparently all immature (JC, 307.01001–8), Quicksand, Kentucky, June 25, 1925. Coll. C. R. Crosby.

Remarks. This puzzling collection is doubtfully referred to the present genus and subgenus. In view of the apparent immaturity of all the specimens even this cannot be ascertained with certainty.

Subgenus PAROBISIUM, nov.

Orthotype. *Neobisium* (*Parobisium*) *magnum*, sp. n.

Diagnosis and Remarks. Characterized in the key.

In addition to the forms here described it is quite likely that the following species also pertain to this group:—"*Obisium japonicum,* Ellingsen; *Obisium pygmæum,* Ellingsen; and *Obisium brevifemoratum,* Ellingsen. However, if Ellingsen's opinion as to the very close relation between the last two of these three species and *Microbisium parvulum* (Banks) be sustained, it will be necessary to refer these two at least to *Microbisium,* gen. nov. A decision cannot be rendered in the absence of material.

Key to the Species of Parobisium.

1. Fingers of chela subequal in length to hand; movable finger of chela with 70 marginal teeth at most	2.
Fingers of chela clearly much longer than hand; movable finger of chela with at least 85 marginal teeth	3
2. Posterior margin of carapace with 10 marginal setæ; tergites with 16–18 marginal setæ: large species, 4·5 to 5·0 mm.; from Japan	*magnum,* sp. n.
Posterior margin of carapace with 8 marginal setæ; tergites with 10–12 marginal setæ: smaller species, 2·5 mm.; from Japan	*flexifemoratum,* sp. n.
3. Femur strongly but evenly granulate along its anterior face and 4·3 (in female) times as long as broad; palm of chelicera with eight setæ: from Oregon	*hesperum,* sp. n.
Femur at most weakly granulate along its anterior face, and 3·8 (young female) times as long as broad; palm of chelicera with six setæ: from Japan	*imperfectum,* sp. n.

Neobisium (*Parobisium*) *magnum*, sp. n.

Holotype, ♀ (JC. 389.01001). Coll. F. Silvestri, Oct. 31, 1924, at Moghi (Kyushu), Japan. No further material.

Diagnosis. Sclerotic parts smooth and polished. Fixed finger of chela with 60 marginal teeth; movable finger with 68–70. Carapace subquadrate, with blunt epistomal process; with four large eyes, the anterior pair of which is 1 diameter from the anterior carapacal margin and ⅓ diameter from the posterior pair; chætotaxy 4–10 (26). Tergites with 16–18 and sternites with 16–20 marginal setæ. Spinneret weakly if at all developed; palm of chelicera with 7 setæ. Palpi robust. Trochanter 1·8–1·9 times as long as broad; femur 3·2 times as long as broad, finely granulate along its anterior margin and broadest distally; tibia strongly pedicellate, 2·1 times as long as broad; chela 2·5 times as long as broad; fingers subequal in length to hand. Fingers gape slightly in female at least. Length of expanded female 5·0 mm.

Neobisium (*Parobisium*) *flexifemoratum*, sp. n.

Holotype, ♀ (JC. 325.01001); paratype, ♀ (JC. 325. 01002). Muchogo-o (?), Japan. Coll. June 3, 1925, by Dr. F. Silvestri.

Diagnosis. Sclerotic parts smooth except for the anterior face of the femur, which is finely but evenly granulate. Fixed finger with 49–50, movable finger with 54–56 marginal teeth. Carapace subquadrate, epistomal process obsolete; eyes greatly reduced and apparently absent in some cases (apparently absent in the holotype; four very weakly differentiated eye-spots in paratype); chætotaxy 4–8 (26). Tergites and sternites with 10–12 marginal setæ. Chelicerae more delicately formed than in *magnum*; spinneret present as a low but distinct sclerotic crest; palm with 7 setæ. Palps robust. Trochanter 1·9 times as long as broad; femur 2·6–2·7 times as long as broad, anteriorly slightly granulate, broadest basally; tibia strongly pedicellate, 2·0 times as long as broad; chela 2·7 times as long as broad; fingers subequal in length to hand. Length 2·5 mm.

Remarks. Apparently rather close to "*Obisium*" *pygmæum*, Ellingsen, from which it differs in its larger size, the presence of a clearly developed spinneret, the slightly stouter and clearly curved femur. In *pygmæum* the femur is described as "robust, with a short, robust but distinct stalk, the inner side slightly convex or nearly straight, femur on the whole nearly parallel-sided, straight, not curved."

In *flexifemoratum* it is anteriorly strongly convex and distally concave; exteriorly and basally strongly swollen, slightly concave medianally and strongly inflected distally.

Neobisium (*Parobisium*) *imperfectum*, sp. n.

Holotype, an apparently immature or young female (JC. 325.02001). From same vial of material as *flexifemoratum*. Muchigo-o (?), Japan. Coll. June 3, 1925, by Dr. F. Silvestri.

Diagnosis. Sclerotic parts uniformly smooth. Fixed finger of chela with 76, movable finger with 86 marginal teeth. Carapace much longer than broad, anteriorly somewhat produced and with a weak epistomal process; two pairs of weakly developed eyes, the anterior pair of which is nearly 2 diameters from the anterior carapacal margin and about ½ diameter from the posterior pair; chætotaxy 4–8 (26). Tergites with 11 or 12 and sternites with 14 or 15 marginal setæ. Cheliceræ slender; spinneret a longitudinal sclerotic crest as in *flexifemoratum*; palm with six setæ. Palps slender. Trochanter 2·0–2·1 times as long as broad femur weakly pedicellate and gently clavate, 3·8 times as long as broad; tibia weakly pedicellate and 2·5 times as long as broad; chela 3·4 times as long as broad; fingers much (1·2 times) longer than hand. Length 3·5 mm.

Remarks. The immaturity of the holotype is inferred from the fact that the chætotaxy of the chela is defective, SB and ISB being absent. Nevertheless, other characteristics make the generic and subgeneric placing certain. In the genus *Microbisium*, which normally possesses a reduced chætotaxy in the adult stage, the missing setæ are SB and IST; also the apical maxillary setæ number 3 instead of 4 as in the present species.

All things considered, this species seems most closely related to the American species *hesperum*, nov.

Neobisium (*Parobisium*) *hesperum*, sp. n.

Holotype, ♀ (JC. 454.01001). Cannon Beach, Oregon. Collected July 15, 1927, in the rubble beneath a log above the high-tide line, by Dr. E. C. Van Dyke.

Diagnosis. Fingers of chela with about 86–88 marginal teeth each. Carapace longer than broad, epistomal process absent; eyes 2, weakly developed, and nearly two ocular diameters from the anterior carapacal margin; chætotaxy 4–6 (24). Tergites with about 12 and sternites with 18 marginal setæ. Cheliceræ slender; spinneret present as a short, somewhat translucent, sclerotic process; palm with 8 setæ. Palps slender. Trochanter showing traces of weak granulation, straight behind, 2·7 times as long as broad; femur strongly but evenly granulate, gently clavate, and broadest distally, 4·3 times as long as broad; tibia smooth, slenderly pedicellate, and gently bilaterally convex, 3·1 times as long as broad; chela obovate basally, fingers longer than hand; chela as a whole 3·2 times as long as broad. Length 5·0 mm.

Genus Microbisium, nov.

Orthotype. *Obisium brunneum*, Hagen.

Diagnosis and Remarks. Characterized in key. Interesting because of the small sizes of the included forms and the fact that males are apparently normally absent (at least, so far as can be ascertained from non-histological studies). It is interesting to speculate as to whether or not this signifies parthenogenesis. In addition to the two species here recorded from the United States, "*Obisium*" *brevipalpe*, Redikorzev, from Kamchatka, seems almost certainly to pertain to this genus.

Ellingsen (1909, p. 220), in reporting upon a collection of material from North America, recorded *parvulum*, Banks, with the comment that it was very similar to his *brevifemoratum* and *pygmæum* from Norway and Japan respectively, and suggested further that they all possibly represented the same species. This may be true, although I am personally more inclined to believe that Ellingsen's species are valid and pertain to *Parobisium*. This point cannot be settled until the species in question are re-studied.

Two North American species definitely pertain to this interesting group. They may be separated by means of the following couplet:—

1. Fingers clearly longer than the hand (1·1 to 1·3 times as long); femur 2·9–3·2 times as long as broad .... *brunneum* (Hagen).
Fingers subequal in length to hand (0·97 to 1·03 times as long); femur 2·6 to 2·8 times as long as broad .... *parvulum* (Banks).

Microbisium brunneum (Hagen).

1869. *Obisium brunneum*, Hagen, p. 52.
1895. *Obisium brunneum*, Hagen, Banks, p. 12.

Types. Hagen's original material was from Massachusetts. It is probably preserved in the Museum of Comparative Zoology.

Determination. The determination of this form is probably correct, in spite of Hagen's insufficient original description.

Material examined. Maine: 1 immature ♀ (JC.894.01001), Presque Isle.

New York: 13 ♀ (JC. 30.01001–13), Cortland County; Labrador Pond. 1 ♀ (JC. 47.01001), Eglestons Glen, Yates County. 2 immature ♀ (JC. 51.01001 and 380.01001), Ithaca. 3 ♀ (JC. 50.01001–2 and 21.01001), Freeville. 2 ♀ (JC. 45.01001–2), Wilmington Notch, Essex County. 5 ♀ (JC. 377.01001–5), Suffexn, Ramapo Mts. 1 ♀ (JC. 385.01001), from *Woodwardia* swamp, Freeville. 5 ♀, 4 immature (JC. 381.01001–9), Cinnamon Lake, Schuyler County. 6 ♀ (JC. 298.02001–6), Sea Cliff (collected by R. V. Chamberlin). 4 ♀ (JC. 49.01001–4), sifted from moss, Ringwood, Tomkins County. 4 ♀ (JC. 378.01001–4), Montauk Point. 4 ♀ (JC. 379.01001–4), Howard. 1 young ♀ (JC. 382.01001), West Barre. 2 immature ♀ (JC. 387.01001–2), Tuxedo. 3 ♀ (very poor condition) (JC. 48.01001–3), Enfield Glen, Ithaca (determination doubtful). 1 immature (JC. 41.01001), Penn Yan (determination doubtful). 2 ♀ (JC. 383.01001–2). 6 ♀ from Heath Bog (JC. 384.01001–6), and 3 ♀ (one with discal mass of 13 normally attached eggs) (JC. 396.01001–3), McLean.

Missouri: 4 ♀ (JC. 33.01001–4), Columbia.

Ohio: 4 ♀ (JC. 404.01001–4), "southern part of state."

Virginia: 1 immature (JC. 400·01001), Alberta (determination doubtful).

Washington, D.C.: 4 apparently immature (JC. 332.01001–4), coll. H. C. Barber (determination doubtful; Crosby material).

Georgia: 2 very young (JC. 43.01001–2), Billy's Island, Okefinokee Swamp (determination doubtful).

Locality unknown (presumably eastern United States): 1 specimen (JC. 29.01001), from type-collection of *Obisium parvulum*, Banks, and labelled "co-type," proves to be the present species. 3 ♀ (JC. 405.01001–3).

Unless otherwise indicated, Dr. C. R. Crosby was the collector of the foregoing material. Specimens in Cornell University and author's collections.

Remarks. Occasionally found in company with *parvulum*, from which it is readily separated by the characters given in the key.

Microbisium parvulum (Banks).

1895. *Obisium parvulum*, Banks, p. 12.
1909. *Obisium parvulum*, Banks, Ellingsen, p. 220.

Types. Deposited in the collections of the Museum of Comparative Zoology. Type-locality unknown. Banks suggests Florida as the likely source. From other considerations (of relative distribution) I believe that somewhere in the middle north-east or west is more likely. A so-called co-type of this species (JC. 29.01001), which I have had the privilege of examining, proves to be a typical specimen of *brunneum* (Hagen). In the absence of the balance of Banks's original material, it is impossible to say whether his species will fall as a synonym or not. But since specimens are available which clearly fit his description of *parvulum* and differ from typical *brunneum*, it seems likely that his type-material contained representatives of both species.

Material examined. North Carolina: 3 ♀ and 1 immature (JC. 333.01001–4), Mt. Pisgah (3000 feet elevation), collected 10.19.1923 by C. R. Crosby.

New York: 2 ♀ (JC. 433.02001–2); 1 ♀ (JC. 52.01001), Ithaca (Fall Creek), collected 7.30.1909 by R. V. Chamberlin. 6 ♀ (JC. 396.02001–6), 5.16.1925, and 1 ♀ (JC. 386.01001), in "Heath bog," 5.30.1921, collected by C. R. Crosby, McLean.

Minnesota: 3 ♀ (JC. 395.01001–2 & 395.02001), collected June 22 and July 17, 1924, respectively, by F. C. Fletcher (Crosby-Cornell Collection), Lake Minnetonka.

Colorado: 1 ♀ (JC. 87.01001), from "surface soil or pine duff beneath douglas fir," and 1 ♀ (JC. 89.01001), from "under scrub-oak chapparal in almost pure gravel"; both lots collected by Dr. E. W. Goldsmith from near Alpine Laboratory, Engleman Canyon, Manitou.

Utah: 17 ♀ (JC. 6.01001–17), collected by author and others from damp soil beneath decaying lawn-grass clippings; in small cavities in the soil; city lot near Liberty Park, Salt Lake City.

Material in author's and Cornell University Collections.

Remarks. The Utah and Colorado material seems typical in every way.

Subfamily *IDEOBISIINÆ*, nov.

1891. *Pseudobisiidæ*, L. Balzan, p. 504.
1906. *Pseudobisiinæ*, Hansen, C. With, p. 77.

Type. Genus *Ideobisium*, Balzan.

Diagnosis and Remarks. Characterized in key. Includes three well-marked genera, which are diagnosed in the key. The geographic range of the subfamily as a whole is cosmopolitan, but predominantly northern. The old subfamily name Pseudobisiinæ is untenable, since there is no genus *Pseudobisium*.

Analytical Key to the Genera of the Ideobisiinæ.

1. Maxillaris apicalis acute, with two slender apical setæ (fig. 2 X); T, ST, and SB of movable finger submedianally clustered and scarcely or not at all a single areolar diameter apart	*Ideobisium*, Balzan, p. 36.
Maxillaris apicalis strongly rounded, short, with 3–5 apical setæ (fig. 2 W); chætotaxy of movable finger of chela not as above	2.
2. Spinneret a row of 8–10 stylet-like galeæ (fig. 1 P); setæ large and conspicuous, there being 20–22 marginal tergal setæ; no tactile setæ on distal third of fingers	*Halobisium*, gen. nov., [p. 35.
Spinneret a single simple or branched galea; setæ inconspicuous, there being at most about 12 marginal tergal setæ; at least one or two tactile setæ situated on distal third of fingers (fig. 3 B)........................	*Microcreagris*, Balzan, [p. 23.

Genus MICROCREAGRIS, L. Balzan.

1891. *Microcreagris*, L. Balzan, p. 543.

Type. *Microcreagris gigas*, L. Balzan.

Remarks. As originally defined, *Microcreagris* merged imperceptibly into *Ideobisium*. As here delimited it is a compact and homogeneous group, which includes not only all those species previously described under its head, but most of those described under *Ideobisium* as well. It is evidently a large genus. Seventeen species, most of which are undescribed, are represented in collections now before me.

The genus seems to be truly Holarctic, reaching its maximum development in China, Japan, and the Pacific coast of North America.

The following artificial key will facilitate specific determinations. It is obviously incomplete :—

Key to certain Species of Microcreagris.

1. Fingers "about" * the same length as the hand	2.
Fingers either longer or shorter than hand	3.

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* It cannot be clearly ascertained from the literature just how the relative lengths of finger and hand were taken. It is possible that remeasurement, on the basis of the method here followed, would alter the ratio given in either direction—hence this precaution.

2. Giant species, 7·1 mm. long: femur of palps smooth; cheliceræ longer than carapace, which possesses a strongly developed epistomal process; with 4 prominent eyes: from China ...... *gigas*, L. Balzan, p. 28.
Small species, 2·5 mm. long: femur of palps strongly granulate; cheliceræ much shorter than carapace, which possesses a moderately developed epistomal process; with 2 eyes: from Europe .... *cambridgei* (L. Koch), [p. 30.
3. Fingers of chela clearly shorter than hand (if small European or giant Chinese species, see also couplet 2 *). 4.
Fingers of chela clearly longer than hand (if small European or giant Chinese species, see also couplet 2 *) ...... 7.
4. Large species (6·5 mm.): from California. *magnum* (Banks), p. 28.
Smaller species (5·0 mm. or less): from the Orient .... 5.
5. Fingers of chela longer than carapace; chela thrice as long as broad: from Tibet .... *kaznakovi*, Redikorzev, [p. 28.
Fingers of chela shorter than carapace; chela distinctly less than three times as long as broad: from China or Japan .... 6.
6. Tibia shorter than hand; fingers no longer than breadth of chela; with 4 apical maxillary setæ; marginal teeth of fingers of chela 35–40 .... *brevidigitata*, sp. n., p. 26.
Tibia longer than hand; fingers much longer than breadth of chela; with 5 apical maxillary setæ; marginal teeth of fingers of chela 65–75 .... *silvestrii*, sp. n., p. 27.
7. Palps at least slightly (generally quite conspicuously) granulate, especially along the anterior femoral margin .. 12.
Palps quite smooth, including the anterior femoral margin .... 8.
8. Femur subclavate, attaining its greatest diameter at least slightly anterior of median: western American species.. 9.
Femur clearly broadest on its basal half, becoming thereafter gradually and progressively attenuate distally: eastern American or Oriental species. 10.
9. IT clearly posterior to and hence posteriorly oblique with ET (fig. 3 F); apical maxillary setæ normally 3 (rarely reduced to 2): small species, 3·5 mm. long .... *cingara*, sp. n., p. 29.

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* It cannot be clearly ascertained from the literature just how the relative lengths of finger and hand were taken It is possible that remeasurement, on the basis of the method here followed, would alter the ratio given in either direction—hence this precaution.

IT even with ET, both the same distance from apex of finger; apical maxillary setæ normally 5 (may be reduced to 4 in immature specimens): large species, 5–6 mm. long .... *sequoiæ*, sp. n., p. 28.

10. IT clearly anterior to ET, and hence anteriorly oblique therewith; apical maxillary setæ 5 .... *japonica*, Ellingsen, p. 28.

IT clearly posterior to ET, and hence posteriorly oblique therewith (fig. 3 F, B, etc.); apical maxillary setæ 3 or 4 .... 11.

11. T and ST only 2 or 3 areolar diameters apart; ST situated ⅓ closer to T than SB; femur 2·4 to 2·7 times as long as broad and anteriorly very finely granulate, as may readily be seen by close inspection: small Oriental species, about 2·0 mm. long .... *formosana*, Ellingsen, p. 30.

T and ST 4 or 5 areolar diameters apart; ST situated only slightly nearer T than SB; femur 3·0–3·1 times as long as broad and completely smooth: larger eastern United States species, about 3·0 mm. long .... *atlantica*, sp. n., p. 29.

12. Femur strongly pedicellate and non-clavate, broadest just beyond pedicel. *formosana*, Ellingsen *, p. 30.

Femur weakly pedicellate and clearly clavate in general appearance, attaining its greatest breadth submedially or distad thereof .... 13.

13. Posterior margin of carapace with 8 or 9 setæ: Oriental species .... 14.

Posterior margin of carapace with 6 border-setæ: western American species .... 15.

14. Tibia stoutly pedicellate, the pedicel itself no longer than its own greatest width (fig. 3 R); trochanter 1·9 to 2·0 times as long as broad .... *orientalis*, sp. n., p. 34.

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* *Formosana*, Ellingsen, may be readily separated from *cambridgei* (L. Koch), which it much resembles in certain respects, by means of the following couplet (see also couplet 2):—

12 *a*. IT clearly closer to EST than ET, being much more distant from the apex of the finger than the former (fig. 3 B); 2 eyes; femur prominently granulate: from England .... *cambridgei* (L. Koch), p. 30.

IT closer to ET than EST, being scarcely more distant from apex of finger than the former (fig. 3 F); 4 weak eyes; femur inconspicuously granulate: Oriental species .... *formosana*, Ellingsen, p. 30.

	Tibia slenderly pedicellate, the pedicel itself clearly much longer than its own greatest width (fig. 3 U); trochanter 2·2–2·3 times as long as broad	*lampra*, sp. n., p. 34.
15.	Tibia elongate, 3 or more times as long as broad in male and 2·8 times or more as long as broad in female	16.
	Tibia plainly stouter than indicated above—no more than 2·7 times as long as broad in male, and correspondingly stouter in female	17.
16.	Trochanter with two small but distinct, widely separated, rounded eminences behind; femur of male 4·3 to 4·5 times as long as broad; tibia of male 3·4 to 3·5 times as long as broad; length of male 3·0–3·5 mm.	*hespera*, sp. n., p. 31.
	Trochanter with inconspicuous irregularities behind, but not as in *hespera*; femur of male at most 4·0–4·1 times as long as broad; tibia of male at most 2·9–3·0 times as long as broad; male 2·0–2·5 mm. long	*duncani*, sp. n., p. 33.
17.	Tibia clearly longer than fingers of chela; EB and ESB arising from summits of small rounded tubercles: from eastern United States	*rufulum* (Banks), p. 30.
	Tibia barely equal to or shorter than fingers of chela; EB and ESB not arising from the summits of tubercles: from western United States	18.
18.	Fingers of chela subequal to tibia in length	19.
	Fingers of chela clearly longer than tibia.	20.
19.	Chela of female 3·0–3·1 times as long as broad; tibia 2·5 times as long as broad; carapace clearly longer than tibia; female 3·5 mm. long	*thermophila*, sp. n., p. 32.
	Chela of male 3·8 times as long as broad; tibia 2·7 times as long as broad; carapace and tibia subequal in length; male 1·9–2·0 mm. long	*lauræ*, sp. n., p. 32.
20.	Femur 3·6 times as long as broad; tibia 2·3–2·5 times as long as broad; chela 2·8–2·9 times as long as broad; male about 3·0 mm. long	*phyllisæ*, sp. n., p. 31.
	Femur 3·1–3·7 times as long as broad; tibia 2·6–2·8 times as long as broad; chela 3·3–3·7 times as long as broad; 2·0–2·8 mm. long	*macilentum* (Simon), p. 31.

Microcreagris brevidigitata, sp. n.

Holotype, ♀ (JC. 390.01001), Mte. Kirishima, Japan. Coll. ix.20.1924 by Dr. Silvestri.

Diagnosis. Movable finger of chela with 40–42 and fixed finger with 33 or 34 marginal teeth. Carapace little if any longer than broad, with two pairs of weakly developed eyes, of which the anterior pair is about ¼ ocular diameter from the posterior pair and 1·5–2·0 diameters from the anterior carapacal margin, which bears a weakly developed epistomal process; chætotaxy 4–10 (28). Apical maxillary setæ 4. Tergites with 13 or 14 and sternites with 16–18 marginal setæ; no discal setæ on sternites. Palps short and robust and nearly smooth. Trochanter 1·8 times as long as broad; femur attaining its greatest diameter ⅓ length from base, weakly granulate along its anterior margin, and 2·4 times as long as broad; tibia stoutly pedicellate, the pedicel itself as broad as long, 1·9 times as long as broad; chela 2·3 times as long as broad; hand 1·7 times as long as the short stubby fingers, which are no longer at most than breadth of hand. Length 3·5 mm.

Microcreagris silvestrii, sp. n.

Holotype, ♂ (JC. 399.01001), Ychyhan (China ?); coll. x.24.1925. Paratopotypes, 4 ♂, same collection data (JC. 399.01002–5).

Diagnosis. Chela with 80–85 marginal teeth on movable and 67–73 on fixed finger. Carapace quadrate, with two pairs of well-developed eyes, the anterior pair of which is ¾ ocular diameter removed from the posterior pair and over a diameter from the anterior carapacal margin, which bears a weakly developed epistomal process; chætotaxy 6–9 (32–33). Apical maxillary setæ 5. Tergites with 14 or 15 and sternites with a similar number of marginal setæ; sternites without differentiated discal setæ. Palps moderately stout and largely smooth. Trochanter with well-developed conical protuberance behind, 1·7 times as long as broad; femur broadest submedianally, completely smooth except for a few scattered rounded tubercles, 3·0–3·1 times as long as broad; tibia stoutly pedicellate, pedicel itself as long as broad, 2·1–2·2 times as long as broad; chela 2·4–2·6 times as long as broad; fingers clearly shorter than hand, but much longer than its breadth. Length of male about 4·0 mm.

Remarks. The holotype shows a very interesting abnormality in the abdominal segmentation. The tergites are completely normal in appearance, but the left half of the seventh sternite only is present. Medianally the fragmentary sternite "pinches out," and the right side possesses no trace of the missing part.

Microcreagris magnum (Banks).

1909. *Ideobisium magnum*, Banks, p. 306.

Remarks. I have not seen material of this species, which is undoubtedly a member of the present genus. If Banks's description is correct, it is the only American member of the genus which possesses chelal fingers which are shorter than the hand.

Microcreagris kaznakovi, Redikorzev.

1918. *Ideobisium* (*Microcreagris*) *kaznakovi*, Redikorzev, p. 97, figs.

Remarks. I have not seen material of this species. Redikorzev's description is adequate. It should be easily determined on the basis of the characters given in the key.

Microcreagris gigas, L. Balzan.

1891. *Microcreagris gigas*, L. Bazan, p. 544.

Remarks. I have not seen material of this species. It is interesting principally as the type of the genus. Its large size and enormous cheliceræ should render it readily recognizable.

Microcreagris japonica, Ellingsen. (Fig. 2 BB.)

1907. *Microcreagris gigas*, var. *japonica*, Ellingsen, p. 7.

Material examined. 1 ♂ (JC. 517.01001), coll. by S. Akiyama at Idzu, Japan, June 1910. Deposited in British Museum of Natural History. 1 ♂ (JC. 388,01001), Chofu, China. Coll. xi.11.1924, by Dr. F. Silvestri.

Remarks. Although Ellingsen's characterization of this form is brief, I believe the determination to be correct. I cannot agree with Ellingsen that the species is a "form" of *gigas*.

Microcreagris sequoiæ, sp. n.

Holotype, ♂ (JC. 570.01001), sifted, together with an immature specimen (JC. 570.01002), from rotting leaves in a grove of redwoods (*Sequoia sempervirens*), by author, ix.7.1927; Muir Woods, Marin County, California.

Additional Material. A badly damaged female (JC. 22.01001), collected by Dr. F. R. Blaisdell, vi.16.1922, at Willow Creek, Humboldt County, California, probably pertains to this species.

Diagnosis. Chela with about 65 marginal teeth on movable and 70 on fixed fingers. Carapace subquadrate, with two pairs of well-developed eyes, the anterior pair of which is about ⅓ ocular diameters from the posterior pair and about 1 diameter from the anterior carapacal margin, which bears a well-developed epistomal process; chætotaxy 4–6 (24). Apical maxillary setæ 5. Tergites with about 12 and sternites with about 16 marginal setæ; sternites 7 and 8 with a weakly differentiated median pair of discal setæ. Palps robust and non-granulate. Trochanter with one or two weak apical protuberances behind, 1·7 times as long as broad; femur smoothly clavate, broadest distally, 3·4 times as long as broad; tibia stoutly pedicellate, the pedicel no longer than broad, 2·3 times as long as broad; chela thrice as long as broad; fingers slightly but distinctly longer than hand. Large species, ♂ 5 mm. long.

Microcreagris cingara, sp. n. (Fig. 2 GG; figs. 3 F, R.)

Holotype, ♂ (JC. 245.02001); allotype, ♀ (JC.245.02002); paratopotypes, 2 ♀, 1 immature (JC. 245.02005–7). All collected iii.19.1924, by Dr. Vasco Tanner at St. George, Utah.

Additional Material. 1 ♀ (JC. 436.01001), coll. xi.24.1927 by D. T. Jones as Springfield, Oregon, seems to pertain to this species. The carapace is scarcely if at all longer than broad, and the femur is broadest somewhat more basally than in the type. Otherwise typical.

Diagnosis. Chela with 55–60 marginal teeth on movable and 60 on fixed finger. Carapace a little longer than broad, with two well-developed pairs of eyes, the anterior pair of which is ½ ocular diameters from the posterior pair and 1 diameter from the anterior carapacal margin, which bears a moderately developed epistomal process; chætotaxy 4–6 (24–26). Apical maxillary setæ 2 or 3. Tergites with 12 and sternites with about 15–16 marginal setæ; sternites 7 and 8 with a weakly differentiated pair of median discal setæ. Palps robust and non-granulate. Trochanter almost or quite evenly convex behind, 1·6–1·8 times as long as broad; femur broadest distally, clavate in appearance, and 3·0–3·3 times as long as broad; tibia stoutly pedicellate, the pedicel no longer than broad, 2·1–2·2 times as long as broad; chela 2·7–2·8 times as long as broad; fingers clearly longer than hand. Length 3·5–4·0 mm.

Microcreagris atlantica, sp. n.

Holotype, ♂ (JC. 434.01001); allotype, ♀ (JC. 434.01002). Both from an unlabelled vial included in a general collection of material from the eastern United States, as collected by Dr. R. V. Chamberlin. Paratype, 1 ♀ (JC. 262.01001), "probably from Asheville," North Carolina. Coll. R. V. Chamberlin.

Diagnosis. Chela with 51–54 marginal teeth on movable and 45–48 on fixed fingers. Carapace clearly longer than broad, with two pairs of eyes, the anterior pair of which is less than $\frac{1}{2}$ ocular diameter from the posterior pair and 1 diameter from the anterior carapacal margin, which possesses a well-developed epistomal process; chætotaxy 4–5 or 6 (26). Apical maxillary setæ 4. Tergites with about 12 and sternites with the same number of marginal setæ; sternites without discal setæ. Palpus medium in build and completely smooth. Trochanter with a small rounded protuberance behind, 1·7–1·9 times as long as broad; femur broadest about medianally, clearly pedicellate, and 3·0–3·1 times as long as broad; tibia with robust pedicel, which is clearly as broad as long, 2·1 to 2·3 times as long as broad; chela rather strongly swollen on inner face, 2·8 to 2·9 times as long as broad; fingers very clearly longer than hand. Length 2·3 to 2·8 mm.

Microcreagris formosana, Ellingsen.

1912 (*b*). *Microcreagris granulata*, var. *formosana*, Ellingsen, p. 127.

Material examined. 2 ♀ (JC. 558.01001–2). Labelled simply "*Microcreagris granulata*, Ellingsen, var." The source of this material is not now known to me, but it was received in exchange. This is almost surely a part of Ellingsen's original collection of some 50 specimens from Takao, Formosa.

1 ♀ (JC. 550.02001), coll. C. F. Baker. Mt. Makiling, Luzon, Philippine Islands.

Remarks. The characters given in the key to the species will amply supplement Ellingsen's scanty original data. I feel quite sure that the determination is correct.

Microcreagris cambridgei (L. Koch).

1873. *Roncus cambridgei*, L. Koch, p. 45.
1911. *Obisium* (*Ideoroncus*) *cambridgei*, Koch, Kew, p. 53.

Material examined. A single ♀ in poor condition (JC. 28.01001), from Devon, England, is at hand. Exchange from the British Museum of Natural History.

Microcreagris rufulum (Banks).

1891. *Obisium rufulum*, Banks, p. 166.
1895. *Ideobisium rufulum* (Banks), Banks, p. 11.

Material examined. 2 ♂, 1 ♀, and 1 ⊙ (JC. 7.01001–4), coll. iv.18 (year unknown), at Glen Sligoe, near Washington, D.C; 2 ♂ (JC. 296.02001–2), from Washington, D.C.; 19 ♂ and ♀ (JC. 3.02001–18), Falls Church, Virginia; 1 ♀ (X. 406.01001), v. 1 (year unknown), Great Falls, Virginia. All except first lot from Dr. R. V. Chamberlin.

Microcreagris hespera, sp. n. (Fig. 3 U.)

Holotype, ♂ (JC. 451.01001), Pepperwood Creek, near mouth of Gualala River, Mendocino County, California; coll. viii.24.1928, by B. C. Cain. Paratype, ♂ (JC. 15.01001), Berkeley, California; coll. Dietrich; loan from Cornell University..

Diagnosis. Chela with 79 teeth on movable and 77 on fixed finger. Carapace longer than broad; apparently completely eyeless; without epistomal process; chætotaxy 4–6 (22). Tergites with about 10, sternites with about 12 border-setæ; sternites 7–9 with a submedian pair of clearly differentiated discal setæ. Maxilla with 3 apical setæ. Palpi extremely long and slender, and conspicuously but evenly granulate. Trochanter with an anterior and posterior rounded tubercle behind, 2·6 times as long as broad; femur attenuate, broadest near tip, 4·4 times as long as broad; tibia with a long and slender pedicel, clearly much longer than broad, 3·4 times as long as broad; chela attenuate, fingers greatly longer than hand and nearly four (3·9) times as long as broad. Length of male 3·5 mm.

Microcreagris macilentum (E. Simon).

1878. *Obisium macilentum*, E. Simon, p. 157.

Material examined. ♂ (JC. 529.01001), 9 ♂ and ♀ (JC. 529.01003–11), and 1 ♂ and 3 ♀ (JC. 54.01001–4). All from Claremont, California. Other collection-data unknown.

Remarks. This determination is probably correct. Dr. Louis Fage has kindly compared one of my specimens (JC. 54.01002) with the type, and verifies my conclusion.

Microcreagris phyllisæ, sp. n.

Holotype, ♂ (JC. 376.01001), Coronado, California, on beach in kelp; coll. by Dr. F. R. Blaisdell, i.19.1928. Paratype, ♂ (JC. 9.01001), Eaton's Cave, Los Angeles County, California, May 1913; from R. V. Chamberlin.

Diagnosis. Movable finger of chela with 52 and fixed finger with a similar number of marginal teeth. Carapace scarcely longer than broad, with two pairs of well-developed eyes, the anterior pair of which is about ⅓ ocular diameter from the posterior pair and a scant diameter from the anterior carapacal margin; epistomal process well developed; chætotaxy 4–6 (26). Apical maxillary setæ 4–5. Tergites with 12 and sternites with 16 marginal setæ; sternites 6–8 with a submedian pair of clearly differentiated discal setæ. Palps slender and clearly granulate. Trochanter with median rounded protuberance behind, granulate, and 2·1 times as long as broad; femur evenly granulate, gradually enlarged from pedicel to near tip, and 3·5–3·6 times as long as broad; tibia with slender pedicel, which is clearly longer than broad, granulate, and 2·4–2·5 times as long as broad; chela slender, 3·0–3·2 times as long as broad; fingers much longer than hand. Length of male 3·2 mm.

Remarks. Named for Phyllis Chamberlin.

Microcreagris thermophila, sp. n.

Holotype, ♀ (JC. 547.01001); paratype, ♀ (JC. 547.01002). Under stones on desert hillside, Box Springs Grade, near Riverside, California. Coll. xi.1925, by the author.

Diagnosis. Movable finger of chela with 53–56 and fixed finger with 44 marginal teeth. Carapace plainly somewhat longer than broad and bearing a single pair of weakly developed eyes, which are clearly more than their own diameter from the anterior carapacal margin; epistomal process vestigial; chætotaxy 4–6 (22). Apical maxillary setæ 4. Tergites with 13–14 and sternites with 14 or 15 marginal setæ; sternites 6–8 with a submedian pair of discal setæ. Palps of slender granulate type. Trochanter granulate, with one or two small posterior protuberances, 2·1–2·2 times as long as broad; femur granulate, gently clavate, and broadest distally, 3·4–3·6 times as long as broad; tibia smooth, with a slender pedicel which is slightly longer than broad, 2·4–2·5 times as long as broad; chela swollen much more greatly on inner than outer face, much as in *macilentum*, 3·0–3·1 times as long as broad; fingers much longer than hand. Length of female 2·8–3·5 mm.

Microcreagris lauræ, sp. n.

Holotype, ♂ (JC. 42.01001), Berkeley, California, i.1920. Cornell University Collection.

Diagnosis. Marginal teeth of chela not ascertainable from type. Carapace much longer than broad, plainly narrowed; with two pairs of weakly developed eyes, the anterior pair of which is more than half an ocular diameter from the posterior pair and 1·5 diameters from the anterior carapacal margin; no epistomal process; chætotaxy 4–6 (22). Apical maxillary setæ 4. Tergites with 12 and sternites with 15 or 16 marginal setæ; sternites without definitely differentiated discal setæ. Palps of slender granulate type. Trochanter granulate, with a couple of weak protuberances behind, 2·4 times as long as broad; femur prominently granulate, gently clavate, and broadest distally, 3·8 times as long as broad; tibia granulate, with pedicel which is clearly longer than broad, 2·7 times as long as broad; chela flattened on outer and swollen on inner face, as in *macilentum*, plainly somewhat granulate, 3·6 times as long as broad; fingers much longer than hand. Length of male 1·6 mm.

Remarks. Named for Laura Anne Chamberlin.

Microcreagris duncani, sp. n. (Fig. 3 B.)

Holotype, ♂ (JC. 5.01001); allotype, ♀ (JC. 5.01002); paratypes, 22 ♂ and ♀ (JC. 5.01003–24). Collected by C. D. Duncan and the author, i.1.1923, under stones in damp soil on serpentine outcrop, Jasper Ridge, San Mateo County, California.

Additional Material. 2 ♂ (JC. 56.01001–2), Alhambra Valley, Contra Costa County, California, xii.29 (year unknown). Collections of California Academy of Sciences. 1 ♀ (JC. 46.01001), collected by Dr. F. E. Blaisdell, iv.16.1922, San Antonio Canyon, Alameda County, California.

Diagnosis. Movable finger of chela with 57–64 and fixed finger with 55–63 marginal teeth. Carapace plainly longer than broad, with two pairs of weakly developed eyes, the anterior pair of which is ½ diameter from the posterior pair and 1 diameter from the anterior carapacal margin, which is devoid of an epistomal process; chætotaxy 4–6 (24). Apical maxillary setæ 4. Tergites with 11–12 and sternites with about 16 marginal setæ; sternites without clearly differentiated discal setæ. Palps of slender granulate type. Trochanter almost parallel-sided, with one or two small protuberances behind, 2·4–2·6 times as long as broad; femur granulate, broadest subdistally, 3·7–4·2 times as long as broad; tibia with slender pedicel, which is clearly longer than broad, granulate, 2·8–3·1 times as long as broad; chela slender, somewhat granulate near fingers at least, 3·8–4·2 times as long as broad; fingers much longer than hand. Length 2·2–2·5 mm.

Remarks. Close to *lauræ*, sp. n. The Alameda County specimen has a stouter chela than typical material (3·5 times as long as broad). Named for Carl Dudley Duncan.

Microcreagris lampra, sp. n.

Holotype, ♀ (JC. 398.01001); paratype, ♀ (JC. 398. 01002). Collected ix.27.1924, by Dr. F. Silvestri at Kusang (China ?).

Diagnosis. Movable finger with 81 and fixed finger with 85 marginal teeth. Carapace subquadrate, epistomal process weakly developed; with two pairs of strongly developed eyes, the anterior pair of which is $\frac{1}{3}$ ocular diameters from the posterior pair and 1 diameter from the anterior carapacal margin; chætotaxy 6–8 or 9 (about 30). Apical maxillary setæ 5. Tergites with about 12, sternites with 16 marginal setæ; sternites without discal migrants. Palps of a robust granulate type. Trochanter weakly granulate, distally widened, with a distinct protuberance behind and 1·9–2·1 times as long as broad; femur broadest distally, granulate along its inner face, 3·4–3·6 times as long as broad; tibia weakly granulate, with a stout pedicel which is no longer than broad, 2·3 times as long as broad; chela smooth, equally convex anteriorly and posteriorly, 3·0–3·1 times as long as broad; fingers much longer than hand. Length of ♀ about 5·5 mm.

Remarks. Very closely related to *orientalis*, sp. n. The most striking points of difference are indicated in the key.

Microcreagris orientalis, sp. n.

Holotype, ♀ (JC. 397.01001), coll. ii.22.1925, by Dr. F. Silvestri at Lookay (China ?).

Diagnosis. Movable finger with 80, fixed finger with 87 marginal teeth. Carapace subquadrate, with vestigial epistomal process and two pairs of weakly developed eyes, the anterior pair of which is $\frac{1}{3}$ to $\frac{1}{2}$ ocular diameter from posterior pair and 1·5 diameters from the anterior carapacal margin; chætotaxy 6–8 (28). Apical maxillary setæ 5. Tergites with 12 and sternites with about 15 marginal setæ; sternites without discal migrants. Palps moderately robust and granulate. Trochanter weakly granulate, with protuberances behind, 2·2 to 2·3 times as long as broad; femur moderately granulate, especially anteriorly, broadest distally, 3·6 times as long as broad; tibia with slender pedicel which is clearly longer than broad; weakly granulate, especially along its anterior margin, 2·4 times as long as broad; chela evenly swollen on either face, smooth, 3·3 times as long as broad; fingers much longer than hand. Length of ♀ 4·0 mm.

Remarks. Very close to *lampra*, sp. n. Most important differences are indicated in the key.

Microcreagris sp. uncertain or indeterminable.

Material examined. The following specimens are without question members of the genus, but because of immaturity or mutilation are specifically indeterminable.

2 ⊙ (JC. 44.01001–2), collected in moss, Portland, Oregon, iii.28.1921, by Prof. E. O. Essig. Pertains to the medium-fingered smooth-palped group of species.

2 ♀ (badly crushed) (JC. 55.01001–2), Claremont, California (from Hilton). Pertains to the medium-fingered smooth-palped group of species.

2 ♀ (JC. 8.01001–2) (badly crushed and mutilated), coll. x.4.1908, at Kendric, Idaho. Pertains to the long-fingered granulate-palped group of species. Stanford University Collection.

4 ⊙, JC. 440·02001, 441.01001, 443.02001, and 444.01001). Coll. during June and July of 1928 by Prof. Martha W. Shackleford; one taken in sweeping herbs, one in dead-leaf litter in stand of *Alnus oregona,* two in moss on ground in Douglas fir-forest, Friday Harbour, San Juan Island, Washington State. These specimens quite likely pertain to *cingara,* sp. n.

Genus Halobisium, nov.

Orthotype. *Ideobisium orientale*, Redikorzev.

Diagnosis. Adequately characterized in key. Known from the coast of California; Commander Islands (off coast of Kamchatka) and "Siberia."

Halobisium orientale (Redikorzev). (Fig. 1 P.)

1917. *Ideobisium orientale,* Redikorzev, p. 98, figs. (published 1922).

Material examined. 53 specimens: ♂, ♀, and ⊙ (JC. 1.01001–45 and 2 A to 2 H). All collected under boards, logs, and other "drift" on Salicornia flats, Palo Alto Salt-Marshes (shores of San Francisco Bay), California, in situations where flooding at high-tides occurs. First lot collected by author, fall of 1921. Lot 2 collected by O. Elton Sette in April 1921.

1 ♀ (JC. 185.01001), from under board about five feet above water-level in Salicornia salt-marshes east of Palo Alto, ix.6.1925. A number of additional specimens (JC. 285.01001–5) from the same locality were taken on the under side of large logs in company with isopods, amphipods, and a few marine worms, v.27.1928. 1 ♀ (JC. 324.01001), labelled "Claremont, California," collected by C. F. Baker

(the locality Claremont is certainly an error; the specimen most certainly came from a semi-marine habitat, possibly Laguna Beach). 1 ♂ and 1 ♀ (JC. 431.01001–2), Commander Islands, Siberia; material received from Dr. R. V. Chamberlin. All material at present in author's collection.

Remarks. Redikorzev had four specimens from an unknown locality and one specimen from "Province de l'Oussourie du Sud : lac Reineke."

The determination seems certain. Redikorzev's description and figures are good, and the material from Siberia falls well within the limits of variation found in specimens from San Francisco Bay.

Genus IDEOBISIUM, L. Balzan.

1891. *Ideobisium*, L. Balzan, p. 539.

Genotype. *Ideobisium crassimanum*, L. Balzan.

Diagnosis and Remarks. Adequately characterized in the key. The four widely distributed species known to me may be separated by means of the following key. I have not seen material of the genotype, but there is little doubt but what it and the three others with which it is here associated are congeneric:—

1. Fingers clearly shorter than breadth of hand; hand 1·7 times as long as fingers (femur 2·3 times as long as broad; tibia 1·7 times as long as broad): from Venezuela .... *crassimanum*, Balzan, [p. 37.

Fingers clearly longer than breadth of hand; hand 1·4 or less times as long as fingers .... 2.

2. Subterminal seta suddenly expanded distally into a broad spatulate tip, which is terminally denticulate (fig. 2 CC): from the Seychelles Islands .... *seychellesensis*, sp. n., [p. 38.

Subterminal seta acute, with fine marginal denticulations or short branches (fig. 2 BB) .... 3.

3. Fingers 1·1–1·2 times as long as breadth of chela; hand 1·1–1·3 times as long as fingers; posterior margin of carapace with six setæ; length 1·5–1·8 mm.: from Lesser Antilles .... *balzanii*, With, p. 37.

Fingers 1·2–1·3 times as long as breadth of chela; hand 1·0–1·1 times as long as fingers; posterior margin of carapace with 7 or 8 setæ; length 2·2–2·8 mm.: from New Zealand .... *peregrinum*, sp. n., [p. 37.

Ideobisium crassimanum, L. Balzan.

1891. *Ideobisium crassimanum*, L. Balzan, p. 542.

Remarks. I have not seen material of this species.

Ideobisium balzanii, With.

1905. *Ideobisium balzanii*, C. With, p. 131, figs.

Material examined. ♂ (JC. 12.01001), from St. Vincent, Lesser Antilles, West Indies. Exchange from British Museum. This is apparently one of With's paratypes. In poor condition.

Ideobisium peregrinum, sp. n.

Holotype, ♂ (JC. 94.02001), coll. Robert W. Grimmet, xi.20.1920, under log in beech forest, Days Bay, Wellington, New Zealand; allotype, ♀ (JC. 96.01001), coll. in leaf-mould by Robert W. Grimmet near Wellington, New Zealand; paratype, immature ♀ (JC. 460.01001), from Kingston, Lake Watipu, New Zealand, Hogg coll. Property of British Museum of Natural History.

Diagnosis. Fixed finger of chela with 31–35 and movable finger with 37–40 marginal teeth. Carapace about quadrate, slightly longer than broad; very broad rounded epistomal process present; with two pairs of weakly developed eyes, the anterior pair of which is ½ diameter from the posterior pair and over 1 diameter from the anterior carapacal margin; chætotaxy 4–7 or 8 (22–24). Galea stylet-like and gently recurved. Subterminal setæ with many laterally situated short branches, not at all clavate or spatulate. Palps of typical robust form; non-granulate. Trochanter concave behind, 1·6 times as long as broad; femur strongly pedicellate and nearly as strongly swollen anteriorly as posteriorly, broadest slightly proximad of median, 2·5 to 2·7 times as long as broad; tibia stoutly pedicellate and bilaterally expanded, 1·9–2·0 times as long as broad; chela strongly and bilaterally swollen beyond the sharply differentiated pedicel, 2·5 to 2·8 times as long as broad; fingers distinctly shorter than hand. Length of ♂ 2·2, ♀ 2·8 mm.

Remarks. In spite of the great geographical discontinuity of their ranges, this species is remarkably close to *balzanii*, With.

Ideobisium seychellesensis, sp. n.
(Figs. 1 X, DD; fig. 2 CC.)

Holotype, probably ♀ (JC. 510.01001). Coll. by the Seychelles Expedition of 1908, on the 'Felicete.' Only the type known.

Diagnosis. Appearance typical. Fixed finger of chela with 33, movable finger with 40 marginal teeth. Carapace and abdominal structures unknown (the body of the type-specimen having accidentally been lost in course of preparation for study). Spinneret a gently recurved stylet. Subterminal seta distally flaring into a terminally incised spatula (fig. 2 CC). Palps of typical robust non-granulate form. Trochanter concave behind, 1·8 times as long as broad; femur much more swollen posteriorly than anteriorly, broadest proximad of median, 2·6 times as long as broad; tibia strongly pedicellate and bilaterally swollen, 1·9 times as long as broad; chela more strongly swollen on inner than outer face, 2·3 times as long as broad; fingers clearly a little longer than hand. A small species, but, owing to loss of body previously noted, an exact measurement is unavailable.

Family **Syarinidæ**, nov.

Type. The genus *Syarinus*, J. C. Chamberlin.

Diagnosis and Remarks. Characterized in key. Comprises two distinct subfamilies and three genera, all known thus far only from the western United States. They may be separated by means of the following key:—

Key to Subfamilies and Genera of the Syarinidæ.

I. Subterminal setæ completely simple and acute; femoral articulation of leg iv. plainly oblique (about as in fig. 1 T); galeate spinneret present. (Subfamily SYARININÆ, nov.) .... 2.

Subterminal setæ plainly toothed or dentate; femoral articulation of leg iv. only weakly oblique (about as in fig. 1 X); galea completely absent. (Subfamily CHITRINÆ, nov.) .... *Chitra*, gen. nov.

2. Marginal teeth of movable finger of chela clearly contiguous; T of movable finger present and nearly contiguous with ST; with a single pair of weakly developed eyes or eye-spots .... *Syarinus*, [J. C. Chamberlin.

Marginal teeth of movable finger of chela clearly and widely spaced; T of movable finger absent; with 4 distinct eyes...... *Hyarinus*, [J. C. Chamberlin.

Subfamily *SYARININÆ*, nov.

Type. The genus *Syarinus*, J. C. Chamberlin.

Diagnosis and Remarks. Characterized in key.

Genus SYARINUS, J. C. Chamberlin.

1925. *Syarinus*, J. C. Chamberlin, p. 329.

Orthotype. *Ideoroncus obscurus*, Banks.

Remarks. The genus includes two, and possibly three, species from the western half of the United States.

Syarinus obscurus (Banks).

1893. *Ideoroncus obscurus*, Banks, p. 66.
1925. *Syarinus obscurus* (Banks), J. C. Chamberlin, p. 330.

Material examined. In addition to the material reported by the author in the note cited above, the following material is at hand :—Two specimens (JC. 570.02001–2), sifted from the dead leaves beneath redwoods in Muir Woods, Marin Co., California, coll. by author, ix.7.1927 ; 3 specimens (JC. 438.01001–3), coll. by A. M. Woodbury, viii.29.1927, in Yellowstone National Park, Wyoming.

Remarks. The male sof this species apparently have a very membranous genital apparatus, and in consequence are very difficult to recognize.

The following couplet will permit its easy separation from *granulatus*, sp. n., its closest relative :—

1. Femur completely smooth and non-granulate; femur 2·6 to 2·8 times as long as broad; chela 2·8–3·0 times as long as broad.............. *obscurus* (Banks).
   Femur evenly and distinctly granulate; femur 3·0–3·3 times as long as broad; chela 3·5 times as long as broad......................... *granulatus*, sp. n.

Syarinus granulatus, sp. n. (Fig. 2 H.)

Holotype, ♂ (JC. 86.01001); allotype, ♀ (JC. 88.01001); paratypes, ♂ (JC. 83.01001) and ♀, 2 (JC. 82.01001–2). All collected by Dr. E. W. Goldsmith in surface-soil or pine-duff beneath Douglas fir-trees, Engleman Canyon, near Alpine Laboratory at Manitou, Colorado.

Diagnosis. Movable finger with 49–50 and fixed finger with 39–44 marginal teeth. Carapace longer than broad, with two weakly developed eyes or eye-spots about an ocular diameter from the anterior carapacal margin; with about 12 marginal setæ along its posterior border as in *obscurus*. Tergites and sternites with 16 and 20 border-setæ respectively, as in *obscurus*. Palps relatively slender, trochanter and femur finely and evenly granulate. Trochanter scarcely swollen behind, 2·5 times as long as broad; femur pedicellate, evenly rounded behind, slightly and gradually expanded anteriorly, and with a distinct but gentle distal concavity, broadest about medianally, 3·0–3·3 times as long as broad; tibia with stout pedicel, almost bilaterally swollen, as long as carapace and 2·7 times as long as broad; chela strongly pedicellate and somewhat more strongly swollen on its outer than inner face, side of hand nearly parallel, 3·5 times as long as broad; fingers curved and much shorter than the hand, which is itself about the same length as the tibia. Length 2·8–3·0 mm.

Remarks. Very distinct from, although clearly related to, *obscurus*, Banks.

The species described by Banks as *Ideobisium tibiale* from Colorado is almost certainly a member of the present genus. If so, it is probably rather close to the present species.

Genus Hyarinus, J. C. Chamberlin.

1925. *Hyarinus*, J. C. Chamberlin, p. 327.

Orthotype. *Hyarinus hesperus*, J. C. Chamberlin.

Remarks. This genus is known only from the type-species, which has not been taken since its original discovery. The type-locality of the type-species is Santa Barbara, California (see Chamberlin, *l. c.* p. 328).

Subfamily *Chitrinæ*, nov.

Type. The genus *Chitra*, nov.

Diagnosis and Remarks. Characterized in key. Includes only the monotypic type-genus, which is known thus far only from California.

Genus Chitra, nov.

Orthotype. *Chitra cala*, sp. n.

Diagnosis and Remarks. In addition to the characters indicated in the key, the males of this genus possess a peculiar median sensorium (presumably) on the sixth sternite. It consists of a circular membranous area surrounding a median sclerotic patch and bordered by acute setæ.

The genus is known only from the orthotype, which is a rare Californian species.

Chitra cala, sp. n. (Figs. 2 X, JJ.)

Holotype, ♂ (JC. 276.01001), sifted from leaf-mould and grass-roots taken from under a willow-tree on the banks of San Francisquito Creek, Stanford University Campus, California, collected by author xii.17.1927. Paratypes, 1 ♂, 3 ♀ (JC. 42.01001–4), January 1920, Berkeley, California. The holotype and one ♀ paratype are in the author's collection; the balance of the material is in the Cornell University Collection.

Diagnosis. Marginal teeth of fingers of chela well developed anteriorly and posteriorly and on both fingers, 42–50 marginal teeth on fixed and 48–55 on movable finger. Carapace distinctly longer than broad, with two pairs of weakly developed eyes and no epistomal process; chætotaxy 6–8 (28). Tergites and sternites with 18–20 marginal setæ. Palps slender, all segments but trochanter with definite areas of fine but even granulation. Trochanter with small protuberance behind, 2·1 to 2·2 times as long as broad; femur weakly pedicellate, attaining its greatest breadth subbasally, and maintaining it thereafter almost to the tip, sides subparallel, 3·5–3·8 times as long as broad; tibia slenderly pedicellate, pedicel longer than broad, thereafter bilaterally swollen and distinctly narrowed distally, 2·3–2·4 times as long as broad; chela pedicellate, bilaterally expanded, 3·0–3·2 times as long as broad; fingers much longer than hand and also tibia. Length 2·2 to 3·0 mm.

Family **Hyidæ**, nov.

Type. The genus *Hya*, nov.

Diagnosis and Remarks. Characterized in preceding key. Represented by a single rare genus, confined, so far as present knowledge permits us to say, to the Philippine Islands. Most closely related to the Ideoroncidæ.

Genus HYA, nov.

Orthotype. *Hya heterodonta*, sp. n.

Diagnosis and Remarks. In addition to the characters noted in the diagnosis of the family, the following characters are probably of generic extent:—

Heterodentate, marginal teeth of fingers of chela unequally developed. Chelicerae normal, with a simple stylet-like galea, lamina exterior absent. Eyes four. Femoral articulation of legs iii. and iv. slightly but clearly oblique to the long axis of the compound segment. Femur of legs i. and ii. much longer than patella. Subterminal seta completely simple and unbranched.

Only the orthotype is known.

Hya heterodonta, sp. n. (Fig. 2 KK ; fig. 3 E.)

Holotype, ♂ (JC. 550.04003); allotype, ♀ (JC. 550.04002); paratypes, 7 ♂ and ♀ (JC. 503 A, 550.04001, and 550.04004–8). Mt. Makiling, Luzon, Philippine Islands. C. F. Baker Collection. Four paratypes are deposited in the United States National Museum.

Diagnosis. Chela slender and conspicuously toothed ; fixed finger with 16 acute teeth, which anteriorly are widely spaced ; between the antero-median of these spaced teeth occur from one to three slightly spaced short and rounded smaller teeth (fig. 2 KK) ; movable finger with marginal teeth very weakly developed are nearly absent, apparently of the contiguous type. Carapace slightly broader than long ; without an epistomal process ; with four well-defined eyes, the anterior pair of which is about an ocular diameter from the anterior carapacal margin ; chætotaxy 4–2 (14). Tergites i. and ii. weakly sclerotized, chætotaxy 4 : 4 : 8 : 8 : 8 : 8. Sternites each with about five marginal setæ. Cheliceræ with 6 setæ on palm ; galea very slender and needle-like. Palps slender and smooth. Trochanter excavated behind, calyciform, 2·1–2·2 times as long as broad ; femur curved, broadest distad of median, 3·8–4·1 times as long as broad ; tibia stoutly pedicellate, the pedicel shading gradually into the rather slender tibia proper ; tibia equal to or longer than carapace, scarcely broader than femur, and 2·4–2·8 times as long as broad ; chela slightly expanded exteriorly at pedicel, then nearly straight to tip of fingers, interiorly greatly swollen and convex, 3·2–3·3 times as long as broad ; fingers much longer than hand or tibia, and nearly as long as femur. Length 1·2–1·4 mm.

Family Ideoroncidæ, nov.

Type. The genus *Ideoroncus*, L. Balzan.

Diagnosis and Remarks. Characterized in key. Representatives occur in southern Asia, North America, and South America. The five genera and two subfamilies here recognized may be separated by means of the following key :—

Analytical Key to the Subfamilies and Genera of the Ideoroncidæ.

1. Chela with the normal 12 tactile setæ, of which IB is subbasally situated on the dorsum of the hand (empodia distinctly shorter than tarsal claws (as in fig. 2 J)). (Subfamily Bochicinæ, nov.)	*Bochica*, gen. nov., [p. 43.
Chela with far in excess of the normal 12 tactile setæ (fig. 3 C) (empodia shorter or longer than tarsal claws). (Subfamily Ideoroncinæ, nov.)	2.
2. Dorsal quadrangle of tactile setæ of hand of chela large, the distance between the exterior setæ clearly greater than the basal width of the movable finger (the posterior pair of dorsal tactile setæ clearly median): South American genus	*Ideoroncus*, L. Balzan, [p. 44.
Dorsal quadrangle of tactile setæ of chela small and compact, the distance between the two exterior setæ being distinctly less than the basal width of the movable finger: North American or Asiatic forms (if North American, the two basal setæ of the dorsal quadrangle are clearly distad of median on the hand)	3.
3. Empodium clearly longer than and extending far beyond the tarsal claws (fig. 2 P); empodium simple or divided	4.
Empodium clearly shorter than the tarsal claws and always undivided (fig. 2 J) ..	*Dhanus*, gen. nov., [p. 47.
4. Empodia clearly bifurcate (fig. 2 L); tergites and sternites entire; lamina exterior absent	*Albiorix*, gen. nov., [p. 44.
Empodia simple and undivided (fig. 2 Q, R); tergites and sternites clearly divided into two lateral scutæ each; small lamina exterior present......................	*Shravana*, gen. nov., p. 48.

Subfamily *Bochicinæ*, nov.

Type. *Bochica*, gen. nov.

Diagnosis and Remarks. Characterized in key. Known from the monotypic type-genus, which is West Indian.

Genus Bochica, nov.

Orthotype. *Ideoroncus withi*, J. C. Chamberlin.

Diagnosis and Remarks. Characterized in key. The plainly plicate abdominal pleural membrane associates this rare genus with the Ideoroncidæ rather than the Hyidæ, which it suggests in the normality of the chætotaxy of the chela.

Bochica withi (J. C. Chamberlin).

1905. *Ideoroncus mexicanus*, Banks (misdetermination), C. With, p. 127.
1923 (*b*). *Ideoroncus withi*, J. C. Chamberlin, p. 359 (nom. nov., species described as *Ideoroncus mexicanus*, Banks, by With (*l. c.*)).

Material examined. Through the courtesy of Dr. Susan Finnegan of the British Museum, I have been privileged to examine the specimen upon which With's generally excellent description was based. This specimen, ♀ (JC. 486.01001), has been designated the holotype of the species. It was collected "near Chantilly" (Windward Islands) at 800 feet elevation in fermenting "cocoa-husks."

Subfamily IDEORONCINÆ, nov.

Type. The genus *Ideoroncus*, Balzan.

Diagnosis and Remarks. Characterized, together with its included genera, in the preceding key.

Genus IDEORONCUS, L. Balzan.

1890. *Ideoroncus*, L. Balzan, p. 444.

Genotype. *Ideoroncus pallidus*, L. Balzan.

Remarks. I have been unable to secure material of Balzan's type-species. As a result, the genus must be left inadequately defined. The genus is certainly a valid one, and the only question is as to its relationship to the other genera of the family. In addition to the orthotype it is quite possible that *Ideoroncus gracilis*, Balzan, belongs here.

Ideoroncus pallidus, Balzan.

1890. *Ideoroncus pallidus*, L. Balzan, p. 444, figs.
1910. *Ideoroncus pallidus*, L. Balzan, Ellingsen, p. 395.

Remarks. Balzan's material of this species was from Paraguay. Ellingsen later recorded it from near Rio de Janeiro in Brazil.

Genus ALBIORIX, nov.

Orthotype. *Ideoroncus mexicanus*, Banks.

Diagnosis and Remarks. Adequately characterized in the preceding key. It may be noted that the chela is always considerably broader than deep. The three species of the genus here recognized may be separated by means of the following key:—

1. Margin of fixed finger of chela conspicuously serrate, due to the close-set retro-conical teeth (fig. 2 DD); the movable finger is similarly dentate near its tip .... 2.

Marginal teeth of both fixed and movable fingers largely obsolete, these teeth being extremely broad at the base, with the very low tooth-cap or apex almost vertically above their respective posterior limits (figs. 2 Y, AA); superficially "toothless," except for the venedens .... *edentatus*, sp. n., p. 46.

2. Fixed finger with a total of 30–32 teeth, of which the posterior ones are low and indistinct, being evident only by the spaced projecting tooth-caps (fig. 2 AA); movable finger with 6–8 rather rounded teeth anteriorly, the balance being vestigial; femur and carapace subequal in length: small species, 1·7–2·0 mm. long.. *parvidentatus*, sp. n., [p. 45.

Fixed finger with a total of 48–50 teeth, of which the posteriormost are reduced, but not so conspicuously so as in *parvidentatus*; movable finger with 14–20 pretty well marked acute teeth near tip of finger: larger species, 2·3–2·6 mm. long . *mexicanus* (Banks), [p. 45.

Albiorix mexicanus (Banks). (Figs. 2 F, DD.)

1898. *Ideoroncus mexicanus*, Banks, p. 289.
1923 (*b*). *Ideoroncus mexicanus*, Banks, J. C. Chamberlin, p. 359, figs.

Neotype, ♀ (JC. 370.01001), Las Animas Bay, Lower California, Mexico. The original holotype was destroyed in the San Francisco earthquake of 1906, and hence the foregoing designation, which was made in 1923 by the author. Banks's material was from San Miguel de Horcasitas, Sonora, Mexico.

Material examined. Mexico: Gulf of California; San Esteban Island, ♀ (JC. 110.01001). San Marcos Island, ♀ (JC. 371.01001). California: ♀ (JC. 375.02001), El Centro, coll. xii.12.1927, by Dr. F. R. Blaisdell Utah: ♀ (JC. 245.01001), St. George, coll. iii.19.1924 by Dr. V. M. Tanner. 8 ♂ and ♀ (JC. 449.01001-8, "Straight Wash," coll. iv.20.1928, by "W. J. G." ♂ (JC. 450.01001), Straight Canyon, San Rafael Desert, iv.20.1928, coll. by A. M. Woodbury. ♀ (JC. 437.01001), Bluff, coll. iv.16.1928, by "W. J. G." Last three collections received from Dr. R. V. Chamberlin.

Remarks. The Utah specimens seem to be quite typical.

Albiorix parvidentatus, sp. n.

Holotype, ♂ (JC. 535.02001), Palm Canyon, Riverside

County, California. Coll. by the author under a stone on a desert hillside, iv.5.1925.

Other Material examined. A dead and immature female (JC. 547.01003), together with its cast skin, was taken in a silken moulting-capsule from the underside of a stone on a desert hillside near Riverside, California. Coll. xi.26.1925 by the author.

Diagnosis. Fingers of chela with conspicuous retro-conical teeth anteriorly on both fixed and movable fingers; 30–32 in all on fixed finger, becoming progressively reduced and inconspicuous basally; movable finger with six or seven distal teeth, which are clearly defined but scarcely acute; posterior to these the teeth are very much reduced or wholly absent. Carapace typical, about same length as, or shorter than, the femur or the fingers of the palps. Palps slender, all segments more or less evenly granulate. Trochanter with distinct protuberance behind, as in *mexicanus*, 2·2–2·3 times as long as broad; femur of typical form, 4·0–4·2 times as long as broad; tibia normal, very slightly broader than femur and about 3·1 times as long as broad; chela typical in general appearance, 3·8 times as long as broad; fingers much (1·7 times) longer than hand, and about the same length as the carapace and femur; hand 1·2 times as broad as deep. Length of male 1·7–1·8 mm. A very active and graceful species.

Albiorix edentatus, sp. n. (Figs. 2 Y, AA; fig. 1 C.)

Holotype, ♂ (JC. 266.01003); paratypes, 4 immature females (probably) (JC. 266.01001–2 and 4). Collected singly under large boulders on yellow pine-covered hillside, Santa Isabella Creek, east slope of Mt. Hamilton, California. Coll. by author v.18.1924.

Diagnosis. Chela typical, marginal teeth of fingers much reduced and inconspicuous throughout, but, as usual, somewhat more prominent on the fixed than the movable finger; teeth contiguous, but very broad and strongly retro-cuneate, so that the tooth-caps themselves appear as a widely spaced linear series of minute tubercles along the dental margin of the finger (fig. 2 AA); fixed finger with a total of 30–33 marginal teeth; movable finger with about 27, which are only slightly less developed than those of the fixed finger (fig. 2 Y), unlike the case in *mexicanus* or *parvidentatus*. Carapace normal and about the same length or shorter than the femur. Palp slender and typical in appearance, more or less clearly granulate on all its segments, but less conspicuously so than in *parvidentatus.* Trochanter 2·1–2·3 times as long as broad; femur about as long as or shorter (latter in young specimens) than fingers of chela, about same length as carapace, 4·1 times as long as broad; tibia 3·0–3·2 times as long as broad; chela 3·6 times as long as broad; fingers very much longer than hand, subequal to femur and carapace; hand 1·15–1·20 times as broad as deep. Length of male 2·4 mm.

Remarks. This beautiful and agile form is most nearly related to *parvidentatus,* from which it differs in the dentition of the chela and larger size.

Genus DHANUS, nov.

Orthotype. *Ideoroncus sumatranus,* Redikorzev.

Diagnosis and Remarks. In addition to the characters noted in the key, it may be observed that a small lamina exterior may be present or absent.

The two included species are both south Oriental. They may be separated by means of the following couplet:—

1. Marginal teeth of movable finger weakly developed or obsolete except for the first six or seven; marginal teeth of fixed finger moderately developed throughout; lamina exterior completely absent: small, non-cave-dwelling species, about 2·0 mm. long .... *siamensis* (With), [p. 47.

Marginal teeth of movable finger strongly developed throughout, as well developed as on the fixed finger; small lamina exterior present: large cave-inhabiting species, about 3·5 mm. long .... *sumatranus* [(Redikorzev), p. 47.

Dhanus siamensis (With).

1906. *Ideoroncus siamensis,* With, p. 81, figs.

Remarks. Through the courtesy of Dr. Kai L. Henriksen I have been privileged to examine one of With's original specimens (♂ (JC. 446.01001)), from Klong Salakpet, Siam.

The general form of this species bears a considerable superficial similarity to members of the genus *Albiorix.*

Dhanus sumatranus (Redikorzev). (Fig. 2 FF; fig. 3 C.)

1922. *Ideoroncus sumatranus,* Redikorzev, p. 545, figs.

Material examined. Two ♂ and three ♀ (JC. 103.01001–5), labelled "Batu caves; in the permanently dark places in the caves." Coll. E. Mjöberg.

Redikorzev's type-material came from "Sumatra, Datu Caves, lower cave, dark, 25.i.1913."

As to whether the two foregoing localities are the same I am unable to ascertain. I had presumed that Mjöberg's material was from Borneo. In response to a direct query concerning this point Mjöberg stated that "all specimens are from Northern Sarawak."

Remarks. My material agrees very well with Redikorzev's excellent description. His figure of the chela, however, is erroneous in that it omits the venom-duct of the movable finger.

Genus SHRAVANA, nov.

Orthotype. *Ideoroncus laminatus,* With.

Diagnosis and Remarks. Adequately characterized in key. The longitudinal division of the tergites and sternites is unique in the Neobisioidea. The genotype and only known species is from Siam.

Shravana laminata (With).

1906. *Ideoroncus laminatus,* With, p. 84, figs.

Material examined. Through the kindness of Dr. Kai L. Henriksen I have been privileged to examine one of With's original specimens, ♀ (JC. 445.01001), from Koh Chang, Siam.

[To be continued.]

II.—*On a new Galago from South-east Africa, with a Note on* Otolicnus garnettii, *Ogilby.* By ERNST SCHWARZ.

IN revising the series of Galagos in the British Museum, the following new race has been found to need description. I have much pleasure in naming it after Professor Einar Lönnberg, the distinguished head of the Naturhistoriska Riksmuseum, Stockholm:—

Galago crassicaudatus lönnbergi, subsp. n.*.

Type-locality. Tambarara, Gorongoza Mts., Portuguese East Africa.

Type. ♂, B.M. no. 8. 1. 1. 17. Collected by Major C. H. B. Grant, 23rd April, 1907 (Rudd Coll.).

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* *Galago crassicaudatus,* Thomas and Wroughton, P. Z. S. 1908, p. 166.

Specimens examined. Thirteen, from the type-locality, from Vumba, Gorongoza Mts., and from Melsetter, Rhodesia.

Closely related to *G. c. crassicaudatus* as defined by Thomas*, but darker and with the tail washed with cinnamon-buff.

Upperside grey washed with buffy brown. Colour of arms always distinctly set off from the body-colour, cinnamon-buff; that of the thighs creamy buff. Finger and toes, not the metacarpus, coffee-brown. Lower surface always slightly washed with buffy. Tail always lighter at the tip, distinctly washed with cinnamon-buff. Face very pale, no distinct nasal stripe, but all the hairs in front of the frontal crest fairly pale and generally contrasted with the colour of the crown.

Dimensions of type:—Head and body 287 mm.; tail 371; hind foot 92; ear 57.

Skull: basal length 55. This is a subadult specimen with the basal suture not entirely ankylosed. In a specimen from Vumba (B.M. no. 20. 9. 1. 1, ♂ old) I have taken the following measurements:—Basal length 61·6 mm., upper length 77·1; zygomatic width 51·4; length of upper tooth-row (C–M^3) 27·7; premolar–molar series (P^2–M^3) 22·2.

This local race of Galago is most nearly related to *crassicaudatus*, but is more tinged with brownish or yellowish both above and below, and especially on the tail, has a pale face without distinct markings, and the fingers and toes dark. It is intermediate between *crassicaudatus* and *umbrosus*, to which the Vumba skins have originally been assigned at the British Museum, but differs clearly from the latter, which has a much darker colour above and a greyish tinge below, dark brown hands and feet, and a dark or blackish tail-tip.

The type-specimen of *Otolicnus garnettii*, Ogilby, which Thomas believed to belong to one of the northern races, is a full-grown specimen which lived at the Zoological Gardens, London, for several years. The very small size of its skull, which induced Thomas to deny its southern origin, is, however, probably due to confinement—in fact, the presence of a parietal plate instead of a sagittal crest, the thickness of the bone, the incomplete ossification of the nasals, are exactly the changes one would expect in an animal with ostitis fibrosa, and which frequently interfere with the process of growth itself.

As regards the skin of the specimen (B.M. no. 55. 12. 24. 50), which is in a good condition, only that the tail-tip is missing, it agrees in every detail except size with a specimen from the Cape (B.M. no. 49. 30. 10) and fairly closely with two specimens (B.M. no. 4. 12. 3. 6–7) from the Ngoye Hills, Zululand. It is a brownish, not a buffy and grey animal, its fur is thick and abundant, and, above all, the supraorbital marks are large, as in all the southern animals like *umbrosus* and *lönnbergi*, and not reduced as in the Kenya (*G. c. lasiotis*, Peters) and Zanzibar (*G. c. agisymbanus*, Coquerel) animals. To conclude, the specific name *garnettii*, Ogilby, will have to stand as the subspecific name for the Cape race of *G. crassicaudatus*, with *zuluensis*, Elliot, as a synonym.

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* Ann. & Mag. Nat. Hist. (8) xx. p. 49 (1917).

III.—*New Genera and Species of* Phycitinæ (*Lepidoptera*, Pyralidæ). By Sir George F. Hampson, Bart.

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Genus Africella, nov.

Type, *A. micræola.*

Palpi upturned, slender, the second joint reaching to about middle of frons, the third moderate; frons smooth; eyes large, round; antennæ of male somewhat laminate and and minutely ciliated. Fore wing narrow; vein 2 from near angle of cell; 3 and 5 separate, 4 absent; 6 from upper angle; 9 absent; 10–11 from cell. Hind wing with vein 2 from just before angle of cell; 3 and 5 on a long stalk, 4 absent; the discocellulars oblique and not angled; 6–7 shortly stalked; 8 anastomosing with 7 to near apex.

Africella micræola, sp. n.

♂. Head, thorax, and abdomen reddish brown mixed with grey-white; antennæ fuscous, ringed with white except towards tips; anal tuft white tinged with ochreous. Fore wing grey-white irrorated with fuscous-brown, the costa and terminal area more suffused with fuscous-brown; the antemedial line represented by a small black-brown spot on vein 1; a dark shade from costa to median nervure; two distinct black discoidal points; subterminal line grey-white, almost straight; cilia with a fine dark line near base. Hind wing semihyaline white tinged with brown, the veins and termen browner; cilia with a brown line near base.

Gold Coast, Bibianaha (*Spurrell*), ♂ type. *Exp.* 10 mm.

Africella amydra, sp. n.

♀. Head, thorax, and abdomen dark reddish brown mixed with grey; the antennæ blackish, the palpi, pectus, legs, and ventral surface of abdomen whitish mixed with red-brown, the tarsi black-brown ringed with white. Fore wing grey-white suffused and irrorated with dark reddish brown; the first line medial, whitish defined on outer side by blackish, oblique, sinuous; two distinct black discoidal points; subterminal line whitish defined on inner side by blackish, sinuous. Hind wing semihyaline whitish tinged with red-brown especially on the veins and towards termen; a blackish terminal line; cilia white tinged with red-brown except at base and tips.

Br. E. Africa, Escarpment (*Doherty*), 1 ♀ type. *Exp.* 16 mm.

Genus Taprobania, nov.

Type, *T. glaucochroa.*

Proboscis fully developed, palpi upturned, smoothly scaled, the second joint reaching to just above vertex of head, the third rather long; maxillary palpi filiform; frons smooth, with ridge of scales above; eyes large, round; antennæ of female often simple; tibiæ smoothly scaled. Fore wing narrow, the apex rounded, the termen obliquely curved; veins 2–3 from near angle of cell, downcurved; 4–5 from angle; 6 from below upper angle; 9 absent; 10–11 from cell. Hind wing with the cell about one-third length of wing; vein 2 from angle; 3 and 5 strongly stalked, 4 absent, the discocellulars oblique, not angled; 6–7 stalked; 8 anastomosing with 7 to about three-fourths of wing.

Taprobania glaucochroa.

†*Homœsoma glaucochroa*, Hmpsn. Journ. Bomb. Nat. Hist. Soc. xviii. p. 260 (1908).

Ceylon.

Genus Rhynchephestia, nov.

Type, *R. rhabdotis.*

Proboscis fully developed; palpi downcurved, extending about twice the length of head and moderately scaled below to end of second joint; maxillary palpi slightly dilated with scales; frons smooth; eyes large, round; antennæ of male laminate and thickened towards base, almost simple; tibiæ smoothly scaled. Fore wing narrow, the apex rounded, the termen obliquely curved; vein 2 from close to angle of cell;

3 and 5 separate, 4 on a very long stalk with 5 or absent; 6 from upper angle; 9 absent; 10–11 from cell. Hind wing with vein 2 from well before angle of cell; 3 and 5 separate, 4 absent; the discocellulars inwardly oblique, not angled; 6–7 from upper angle of cell; 8 anastomosing with 7 to three-fourths of wing.

Rhynchephestia rhabdotis, sp. n.

♂. Head and thorax black-brown with a leaden gloss, the vertex of head at sides, genæ, and a ring round neck fulvous, the palpi white to towards extremity of second joint where the white ends obliquely, the antennæ black-brown; abdomen black-brown; pectus, legs, and ventral surface of of abdomen white tinged with brown, the legs with some blackish. Fore wing glossy black-brown; the costal area irrorated with white to beyond middle; a rather diffused white fascia from base through the cell to just beyond it with some white irroration below it and beyond it where it extends to just below the costa. Hind wing dark brown; cilia brownish white with a dark line near base. Underside of fore wing with the inner area whitish; hind wing white tinged with brown.

HAWAII, Maui (*Terry*), 2 ♂ type. *Exp.* 20 mm.
Larva on *Argyroxiphium*.

Genus NEONONIA, nov.

Type, *N. taprobalis*.

Proboscis fully developed; palpi upturned to about vertex of head and smoothly scaled, the third joint as long as the second; maxillary palpi filiform; frons smooth; eyes large, rounded; antennæ of male almost simple; tibiæ smoothly scaled. Fore wing narrow, the apex rounded, the termen evenly curved; vein 2 from well before angle of cell; 3 and 5 shortly stalked, 4 absent; 6 from below upper angle; 9 absent; 10–11 from cell. Hind wing with vein 2 from well before angle of cell; 3 and 5 strongly stalked, 4 absent; the discocellulars erect and slightly angled, 6–9 shortly stalked; 8 anastomosing with 7 to three-fourths of wing.

Neononia taprobalis.

Nonia taprobalis, Hmpsn. Journ. Bomb. Nat. Hist. Soc. xviii. p. 259 (1907).

CEYLON.

Genus UNADILLIDES, nov.

Type, *U. distichella.*

Proboscis fully developed; palpi obliquely upturned, extending to about the vertex of head and moderately fringed with scales below; maxillary palpi slightly dilated with scales at extremity; frons smooth; eyes large, round; antennæ of male somewhat annulate and almost simple; tibiæ smoothly scaled. Fore wing narrow, the apex rounded, the termen obliquely curved; vein 2 from towards angle of cell; 3 and 5 separate, 4 absent; 6 from upper angle; 9 absent; 10–11 from cell. Hind wing with vein 2 from near angle of cell; 3 and 5 strongly stalked, 4 absent; the discocellulars angled; 6–7 stalked; 8 anastomosing with 7 to near apex.

Unadillides distichella.

Homœosoma distichella, Meyr. Pr. Linn. Soc. N.S.W. iii. p. 215 (1878); Rag. Rom. Mém. viii. p. 262, pl. 39. f. 20.

QUEENSLAND; N.S. WALES; VICTORIA.

Unadillides microphæa, sp. n.

Head and thorax dark red-brown mixed with some whitish; abdomen whitish suffused with red-brown; tarsi dark brown ringed with white. Fore wing dark red-brown irrorated with whitish, the terminal area rather darker; a whitish medial line, excurved in submedian interspace; a whitish subterminal line incurved below costa and at submedian fold; cilia with a white line at base. Hind wing ochreous-white tinged with red-brown especially towards termen, the veins red-brown; cilia with an ochreous-white line at base.

SIERRA LEONE (*Clements*), 2 ♂ type. *Exp.* 10–12 mm.

Genus NASUTES, nov.

Type, *N. venata.*

Proboscis fully developed; palpi downcurved, about three times length of head and moderately scaled below; maxillary palpi filiform; frons smooth; eyes large, round; antennæ of male ciliated; tibiæ smoothly scaled. Fore wing narrow, the apex rounded, the termen obliquely curved; vein 2 from long before angle of cell; 3 and 5 separate, 4 absent; 6 from upper angle; 9 absent; 10–11 from cell. Hind wing with vein 2 from near angle of cell; 3 and 5 strongly stalked, 4 absent; the discocellulars strongly angled; 6–7 stalked; 8 anastomosing with 7 to near apex.

Nasutes venata, sp. n.

♂. Head and thorax whitish tinged with brownish ochreous, the shoulders and outer part of patagia fuscous, pencilled with white, the antennæ blackish below, the palpi fuscous pencilled with white; abdomen white suffused with fuscous leaving white segmental lines, the anal tuft ochreous-white; pectus, legs, and ventral surface of abdomen white mixed with fuscous. Fore wing brownish ochreous, the costal area white irrorated with black, the veins white defined by black formed by streaks of black scales; cilia white mixed with fuscous. Hind wing white strongly tinged with fuscous-brown, the cilia whiter.

U.S.A., Colorado, Boulder (*Cockerell*), 1 ♂ type. *Exp.* 20 mm.

Genus CHRYSOSCINIA, nov.

Type, *C. plicata.*

Proboscis fully developed; palpi upturned, the second joint reaching to about vertex of head and moderately scaled, the third nearly as long as the second and with triangular tuft of scales in front; frons smooth, with tuft of scales above; eyes large, round; antennæ of male somewhat laminate and almost simple; the vertex of head tufted with scales; tibiæ smoothly scaled; abdomen of male long and with lateral tufts of scales on medial segments. Fore wing narrow, the costa moderately arched, the apex rounded, the termen evenly curved; vein 2 from long before angle of cell, curved; 3 from well before angle; 4–5 from angle, in line with the median nervure; 6 from upper angle; 8, 9, 10 stalked; 11 from cell. Hind wing with the cell about one-third length of wing; vein 2 from just before angle of cell; 3 and 5 stalked, 4 absent; the discocellulars angled; 6–7 shortly stalked; 8 anastomosing with 7; the male with a strong fold thickened by a ridge of scales just below the cell extending to about three-fourths of wing.

Chrysoscinia plicata, sp. n.

Head and thorax pale rufous, the frons and ridge of scales above it black in male, the antennæ fuscous, the palpi with the third joint black; abdomen golden orange, the basal segment pale rufous; pectus and legs pale reddish brown, the tibiæ and tarsi banded with fuscous. Fore wing flesh-colour suffused with dark purple-brown; short oblique blackish streaks from base of costa and median nervure; antemedial line almost medial, rather diffused blackish with some silvery-white scales on its outer edge, strongly angled outwards below costa at median nervure and above inner margin; subterminal line white defined on inner side by blackish brown, slightly excurved at middle; an orange line at base of cilia. Hind wing orange, strongly suffused with brown except on inner area and cilia.

BR. N. GUINEA, Milne Bay (*Meek*), 1 ♂, 1 ♀ type. *Exp.* 16 mm.

C ✓ Genus MESCINIELLA, nov.

Type, *M. micans.*

Proboscis fully developed; palpi upturned, the second joint reaching to vertex of head, in male rather broadly scaled in front, in female moderately scaled, the third in male short and thickly scaled, in female as long as the second joint and smoothly scaled; maxillary palpi filiform; frons rather hollowed out in centre in male, smooth in female; eyes large, round; antennæ of male somewhat laminate and almost simple; fore and mid tibiæ smoothly scaled, the hind tibiæ with tuft of hair above at extremity. Fore wing narrow, the costa rather strongly arched towards apex which is rounded, the termen evenly curved; veins 2 and 3 stalked from well before angle of cell, curved; 4–5 from angle; 6 from upper angle; 8 and 10 stalked, 9 absent; 11 from cell. Hind wing with the cell about one-third length of wing; vein 2 from well before angle of cell; 3 and 5 stalked, 4 absent; the discocellulars curved; 6–7 shortly stalked; 8 anastomosing with 7 to near apex; the male with a large lobe at base of costa, its extremity tufted with hair, a fringe of hair beyond it for a short distance just below the costa.

Mesciniella micans.

Euzophera micans, Hmpsn. Moths Ind. iv. p. 74 (1896); id. Rom. Mém. viii. p. 86, pl. 48. f. 3.

CEYLON.

C ✓ Genus CAUSTELLA, nov.

Type, *C. micralis.*

Proboscis fully developed; palpi upturned, the second joint reaching to about middle of frons and moderately scaled in front, the third moderate and thickly scaled except at tips; maxillary palpi filiform; frons smooth, without tuft of scales; eyes large, round; antennæ of male minutely ciliated; mid and hind tibiæ moderately fringed with hair. Fore wing rather narrow, the apex rounded, the termen evenly curved; vein 2 from well before angle of cell, 3 from angle; 4–5 shortly stalked; 6 from upper angle; 8–9 stalked; 10–11 from cell. Hind wing with the cell about half the length of wing; vein 2 from well before angle of cell; 3 and 5 on a long stalk, 4 absent; the discocellulars straight and erect; 6–7 from upper angle; 8 anastomosing with 7 to near apex.

Caustella micralis.

Heterographis micralis, Hmpsn. Moths Ind. iv. p. 70 (1896); id. Rom. Mém. viii. p. 28, pl. 48. f. 19.

TRANSVAAL; NATAL, Durban in coll. Janse; CEYLON.

Caustella phœnicias, sp. n.

Head and thorax black glossed with leaden grey usually with more or less purplish red near extremity of the patagia; abdomen grey tinged with fuscous and with some ochreous at extremity; pectus and legs grey suffused with black, the tarsi ringed with white. Fore wing with the basal half purple-red, the costa suffused with black and irrorated with silvery-grey scales; an ill-defined ochreous band tinged with red just beyond middle, narrowing to costa; the rest of wing black irrorated with silvery-grey and with a narrow purple-red subterminal band not reaching the costa. Hind wing grey tinged with fuscous; a dark terminal line and whitish line at base of cilia.

TRANSVAAL, Pretoria (*Janse*), 1 ♂, 3 ♀ type. *Exp.* 12–14 mm.

Caustella strigifera, sp. n.

Euzophera cinerosella, Hmpsn. Mon. Christmas I. p. 73 (nec Zell).

Head, thorax, and abdomen white mixed with red-brown. Fore wing white suffused with red-brown and slightly irrorated with blackish, the costal area whiter to near apex where it tapers to a point; a black streak below basal part of costa and slight streak below the cell near base; a medial black point on median nervure; an obscure white discoidal bar defined by black scales and with black streaks just before and beyond it on the veins to near termen, interrupted except towards costa by the indistinct whitish subterminal line which is oblique below vein 4; a terminal series of black points. Hind wing whitish suffused with red-brown, the cilia whiter.

CHRISTMAS I. (*Andrewes*), 1 ♂, 1 ♀ type. *Exp.* 18 mm.

Genus MASCELIA, nov.

Type, *M. ectophæa*.

Proboscis fully developed; palpi upturned, the second joint reaching to about middle of frons and rather broadly scaled in front, the third long and thickly scaled to near tip; maxillary palpi dilated with scales; frons smooth; eyes large, round; antennæ of male strongly laminate and almost simple; fore and mid tibiæ smoothly scaled, the hind tibiæ with tuft of hair above at extremity; abdomen with lateral tufts of scales. Fore wing narrow, the apex rounded, the termen evenly curved; vein 2 from towards angle of cell, curved; 3 from just before angle; 4–5 from angle, not in line with the median nervure; 6 from angle; 8, 9, 10 stalked; 11 from cell. Hind wing with the cell about half the length of wing; vein 2 from well before angle of cell; 3 and 5 from angle, 4 absent; the discocellulars curved; 6–7 shortly stalked; 8 anastomosing with 7.

Mascelia ectophæa.

Euzophera ectophæa, Hmpsn. Journ. Bomb. Nat. Hist. Soc. xviii. p. 262, pl. E. f. 19 (1908).

CEYLON.

Genus PHESTINIA, nov.

Type, *P. costella*.

Proboscis fully developed; palpi upturned, moderately scaled, the second joint reaching to about vertex of head, the third long; maxillary palpi dilated with scales and flattened against the frons which is smooth and with a tuft of hair above; eyes large, round; antennæ of male with slight tufts of scales at the joints; tibiæ slightly fringed with hair. Fore wing narrow, the apex rounded, the termen evenly curved; vein 2 from just before angle of cell, oblique; 3 and 5 stalked, 4 absent; 6 from upper angle; 8–9 stalked; 10–11 from cell. Hind wing with the cell about one-third length of wing; vein 2 from middle of cell; 3 and 5 from angle, 4 absent; the discocellulars oblique; 6–7 stalked; 8 anastomosing with 7 almost to apex.

Phestinia costella, sp. n.

♂. Head red-brown; thorax and abdomen red-brown mixed with white; pectus, legs, and ventral surface of abdomen white mixed with some red-brown, the tarsi red-brown ringed with white. Fore wing whitish suffused with red-brown, the costal area nearly pure white with the costal edge brown towards base, the terminal area slightly suffused with red-brown and with dark streaks below veins 6, 5, 3; the first line almost medial, oblique to median nervure where it is angled outwards, then inwardly oblique; two blackish discoidal points; subterminal line indistinct, whitish defined on inner side by brown, oblique; a slight dark terminal line. Hind wing white suffused with reddish brown, the cilia nearly pure white.

JAMAICA, Constant Springs (*Walsingham*), 1 ♂ type. *Exp.* 20 mm.

Genus SYMPHESTIA, nov.

Type, *S. ephestialis.*

Proboscis fully developed; palpi upturned, moderately scaled, the second joint reaching to about middle of frons, the third moderate; maxillary palpi minute and slightly dilated with scales; frons smooth; eyes large, round; antennæ of female somewhat laminate and almost simple; tibiæ smoothly scaled. Fore wing rather narrow, the apex rounded, the termen evenly curved; vein 2 from well before angle of cell, oblique; 3 and 5 from angle, 4 absent; 6 from upper angle; 8, 9, 10 stalked; 11 from cell. Hind wing with the cell about half the length of wing; vein 2 from well before angle of cell; 3 and 5 stalked, 4 absent; the discocellulars oblique; 6–7 shortly stalked; 8 strongly anastomosing with 7.

Symphestia ephestialis.

Euzopherodes ephestialis, Hmpsn. Journ. Bomb. Nat. Hist. Soc. xv. p. 24 (1903).

SIKHIM.

Genus JACUTSCIA, nov.

Type, *J. strigata.*

Proboscis fully developed; palpi downcurved, extending about twice the length of the head and thickly scaled; maxillary palpi of male brush-like in a fold of the labial palpi; frons with slight conical prominence with raised edges; eyes large, round; antennæ of male with the basal joint long, the shaft laminate and almost simple, with a sinus at base containing slight scale-like teeth; tibiæ smoothly scaled. Fore wing rather narrow, the costa evenly arched, the apex rounded, the termen obliquely curved; vein 2 from towards angle of cell, curved; 3 from angle; 4 absent; 5 not in line with the median nervure; 6 from upper angle; 8, 9, 10 stalked; 11 from cell. Hind wing with the cell about half the length of wing; vein 2 from angle of cell; 3 and 5 strongly stalked, 4 absent; the discocellulars obliquely curved; 6–7 stalked; 8 anastomosing with 7.

Jacutscia strigata, sp. n.

♂. Head, thorax, and abdomen ochreous-white mixed with some pale red-brown; pectus, legs, and ventral surface of abdomen ochreous-white irrorated with brown. Fore wing ochreous-white with diffused streaks of dark brown irroration along the veins. Hind wing grey-brown, the cilia whitish with a brown line near base. Underside grey-brown.

N. SIBERIA, Schigansk, 1 ♂ type. *Exp.* 30 mm.

Genus ETHIOPSELLA, nov.

Type, *E. nasuta.*

Proboscis fully developed; palpi downcurved, extending about three times length of head, the second joint thickly scaled above; maxillary palpi slightly dilated with scales; frons smooth; eyes large, round; antennæ of female almost simple, the basal joint rather long; tibiæ smoothly scaled. Fore wing narrow, the apex rounded, the termen obliquely curved; vein 2 from well before angle of cell, oblique; 3 and 5 from angle, 4 absent; 6 from upper angle; 8, 9, 10 stalked; 11 from cell. Hind wing with the cell about half the length of wing; vein 2 from just before angle of cell; 3 and 5 on a long stalk, 4 absent; the discocellulars curved; 6–7 from upper angle; 8 anastomosing with 7 to about three-fourths of wing.

Ethiopsella nasuta, sp. n.

♀. Head and thorax grey-brown mixed with some pale reddish; abdomen grey-brown; pectus, legs, and ventral surface of abdomen dark brown mixed with whitish, the tarsi black-brown ringed with white. Fore wing grey-brown mixed with some pale reddish and with obscure dark streaks on the veins; an indistinct dark antemedial line from cell to inner margin, small discoidal spot, and oblique postmedial line slightly incurved at submedian fold. Hind wing semihyaline white, the costa slightly tinged with brown; a fine brown terminal line and line near base of cilia.

S. NIGERIA, Baro (*Simpson*), 1 ♀ type. *Exp.* 20 mm.

Genus OGILVIA, nov.

Type, *O. pulverealis*.

Proboscis fully developed; palpi downcurved, extending about three times length of head and thickly scaled; maxillary palpi dilated with scales and appressed to the frons which is rounded and with a tuft of scales; eyes large, round; antennæ of male somewhat laminate and almost simple; fore and mid tibiæ smoothly scaled, the hind tibiæ with slight tufts of hair above at base and extremity. Fore wing rather narrow, the apex rounded, the termen evenly curved; vein 2 from well before angle of cell, oblique; 3 from just before angle; 4–5 from angle, not in line with the median nervure and approximated for some distance; 6 from upper angle, 8–9 stalked; 10–11 from cell. Hind wing with the cell about half the length of wing; vein 2 from near angle of cell which is produced; 3 and 5 from angle and approximated for some distance, 4 absent; the discocellulars curved; 6–7 from upper angle; 8 not anastomosing with 7.

Ogilvia pulverealis.

Hypogryphia pulverealis, Hmpsn. Bull. Liverp. Mus. ii. p. 39 (1899); id. Nat. Hist. Sokotra, p. 333, pl. xx. f. 16.

SOKOTRA.

Genus ŒDOTHMIA, nov.

Type, *Œ. endopyrella*.

Proboscis fully developed; palpi upturned, the second joint reaching to well above vertex of head and moderately scaled, the third moderate and thickly scaled; maxillary palpi triangularly scaled and flattened against the frons, which has a thickly scaled pointed conical prominence; eyes large, round; antennæ of male somewhat laminated and almost simple, the basal joint rather large, the shaft very slightly excised at base; tibiæ smoothly scaled. Fore wing narrow, the apex rounded, the termen obliquely curved; vein 2 from just before angle of cell, curved and closely approximated to 3; 3 and 5 from angle, 4 absent; 6 from upper angle; 8–9 stalked; 10–11 from cell. Hind wing with the cell about half the length of wing, its lower extremity produced; vein 2 from just before angle of cell; 3 and 5 strongly stalked; the discocellulars very oblique; 6–7 shortly stalked; 8 anastomosing with 7 to about three-fourths of wing.

Œdothmia endopyrella, sp. n.

Eurythmia ignidorsella, Druce, Biol. Centr.-Am., Het. ii. p. 565 (part.), nec Rag.

♂. Head, tegulæ, and patagia whitish tinged with pale red, the outer edge of patagia and dorsum of thorax black, the antennæ blackish above, the palpi pale red, whitish in front, the third joint blackish; abdomen brownish white with some black at base; pectus and legs pale red mixed with some white. Fore wing black-brown; a white costal fascia irrorated with pale red, narrowing to a point at apex: a few silvery scales above medial part of vein 1 and near end of cell; two pale fulvous-red spots on inner medial area, conjoined below vein 1. Hind wing white with some brown suffusion on terminal area except towards tornus and a dark terminal line; cilia white with a brownish line near base.

Mexico, Vera Cruz, Atoyac (*Schumann*), 1 ♂ type Godman-Salvin Coll. *Exp.* 18 mm.

Genus Synothmia, nov.

Type, *S. bahamasella.*

Proboscis fully developed; palpi upturned, the second joint reaching to well above vertex of head and moderately scaled, the third moderate and thickly scaled; maxillary palpi of female filiform; frons smooth; eyes large, round; antennæ of female almost simple, the basal joint rather long, the shaft very slightly excised at base; tibiæ smoothly scaled. Fore wing narrow, the apex rounded, the termen obliquely curved; vein 2 from close to angle of cell, curved; 3 and 5 from angle, 4 absent; 6 from upper angle; 8–9 stalked; 10–11 from cell. Hind wing with the cell about half the length of wing, its lower extremity strongly produced; vein 2 from just before angle of cell; 3 and 5 strongly stalked, 4 absent; the discocellulars strongly angled; 6–7 from upper angle; 8 anastomosing with 7 to about three-fourths of wing.

Synothmia bahamasella, sp. n.

♀. Head and thorax dark reddish brown mixed with some grey-white, the antennæ blackish, the palpi whitish to middle of second joint, then blackish; abdomen reddish brown, obscurely banded with grey-white, the anal tuft ochreous; pectus, legs, and ventral surface of the abdomen dark brown mixed with grey-white. Fore wing black-brown with a few silvery-white scales, the costal area white irrorated with pale red, extending in end of cell to discal fold, then narrowing to apex, a small red spot on it at upper angle of cell; some pale red on basal inner area and a patch on medial area from submedian fold to inner margin, its outer edge oblique, the antemedial line represented by the dark area between these two patches and a small white spot on vein 1; a minute white spot at lower angle of cell; an oblique silvery-white subterminal line. Hind wing white tinged with brown especially on terminal area; a dark terminal line; cilia whitish with a brown line through them.

BAHAMAS, Nassau (*Sir G. Carter*), 1 ♀ type. *Exp.* 16 mm.

Genus CAYENNIA, nov.

Type, *C. rufitinctalis.*

Proboscis fully developed; palpi upturned, the second joint reaching to about middle of frons and slenderly scaled in front, the third moderate; maxillary palpi filiform; frons smooth; eyes large, round; antennæ of male somewhat laminate and minutely ciliated; tibiæ slightly fringed with hair. Fore wing rather narrow, the costa arched towards apex which is rounded, the termen obliquely curved; vein 2 from towards angle of cell, curved; 3 from before angle; 4–5 stalked, not in line with the median nervure; 6 from below upper angle; 8, 9, 10 stalked; 11 from cell. Hind wing with the cell about half the length of wing; vein 2 from just before angle of cell; 3 and 5 strongly stalked, 4 absent; 6–7 stalked; 8 anastomosing with 7 to near apex.

Cayennia rufitinctalis, sp. n.

♂. Head and thorax grey mixed with brown; abdomen grey suffused with fuscous-brown. Fore wing grey, irrorated with fuscous, the basal half of inner area and the tornal half of terminal area tinged with rufous; medial line whitish defined on each side slightly by rufous and with minute black streaks before and beyond it on the veins; black points at angles of cell and others on bases of veins 2–3; postmedial line very indistinct; pale, defined by black marks before and beyond it on costa and minute black streaks before it on the veins; a terminal series of black points. Hind wing semihyaline whitish tinged with brown, especially on the veins and terminal area.

FR. GUIANA, Cayenne (*Schaus*), 1 ♂ type. *Exp.* 18 mm.

Genus Penetiana, nov.

Type, *P. proleucia.*

Proboscis fully developed; palpi upturned to just above vertex of head, smoothly scaled, the third joint moderate; maxillary palpi filiform; frons smooth; eyes large, round; antennæ of male somewhat laminate and almost simple; tibiæ smoothly scaled. Fore wing narrow, the apex rounded, the termen obliquely curved; vein 2 from well before end of cell, oblique; 3 and 5 from angle, 4 absent; 6 from upper angle; 8–9 stalked; 10–11 from cell, 10 closely approximated to 8–9. Hind wing with the cell about half the length of wing, its lower angle produced; vein 2 from angle; 3 and 5 strongly stalked, 4 absent; the discocellulars angled; 6–7 stalked; 8 anastomosing with 7 to towards apex.

Sect. I.—Antennæ of male with the shaft excised towards base and with slight scale-teeth in the excision.

Penetiana penthetria, sp. n.

♂. Head, thorax, and abdomen black with a leaden gloss; tarsi ringed with white; ventral surface of abdomen black irrorated with white, the sides and terminal segments white tinged with brown. Fore wing black-brown glossed with leaden grey; antemedial line silvery grey, oblique; a slight white discoidal bar; subterminal line silvery grey, slightly incurved below costa. Hind wing semihyaline white, the costal area suffused with fuscous; a fine black terminal line except towards tornus. Underside of fore wing whitish suffused with fuscous except on inner area.

Port. E. Africa, M. Chiperone (*Neave*), 1 ♂ type. *Exp.* 26 mm.

Sect. II.—Antennæ of male without sinus at base of shaft.

Penetiana proleucia, sp. n.

Head and thorax pale brown mixed with whitish; abdomen white tinged with ochreous-brown, the ventral surface brown. Fore wing whitish suffused and irrorated with brown, the costal area white except towards base, ill-defined below; subterminal line indistinct, whitish defined on inner side by brown, somewhat angled outwards below costa, then oblique; a dark terminal line and fine white line at base of cilia. Hind wing white slightly tinged with brown; a fine brown terminal line.

S.E. Borneo (*Doherty*), 1 ♂ type; Philippines, Luzon, Mt. Makiling (*Baker*), 1 ♀. *Exp.* 16 mm.

Genus AUCHMERA, nov.

Type, *A. falsalis.*

Proboscis fully developed; palpi obliquely upturned, moderately scaled, the second joint reaching to about vertex of head, the third short; maxillary palpi filiform; frons smooth; eyes large, round; antennæ of male with the basal joint long and thickly scaled, the shaft with sinus at base, strongly ciliated; tibiæ smoothly scaled, the mid-tibiæ of male dilated with a fold containing a tuft of hair. Fore wing narrow, the apex rounded, the termen evenly curved; vein 2 from near angle of cell, curved; 3 from angle; 4–5 strongly stalked in line with the median nervure; 6 from upper angle; 8–9 stalked; 10–11 from cell. Hind wing with the cell about half the length of wing; vein 2 from angle of cell; 3 and 5 strongly stalked, 4 absent; the discocellulars obliquely curved; 6–7 stalked; 8 not anastomosing with 7.

Auchmera falsalis.

Heterographis falsalis, Hmpsn. Journ. Bomb. Nat. Hist. Soc. xviii. p. 261 (1908).

MADRAS, Gooty.

Auchmera yezonis, sp. n.

♂. Head, thorax, and abdomen pale red-brown; pectus and legs red-brown mixed with some white. Fore wing greyish suffused with red-brown; antemedial line indistinct, sinuous, pale with tufts of raised blackish scales on its outer side in and below the cell; slight dark medial marks on median nervure and at inner margin; an indistinct oblique diffused brown postmedial line. Hind wing white suffused with red-brown; a dark terminal line and fine white line at base of cilia.

JAPAN, Yezo, Hakodaté (*Andrews*), 1 ♂ type. *Exp.* 24 mm.

Auchmera melanodes, sp. n.

♀. Head and thorax black-brown suffused with grey-white; abdomen fuscous with brownish-white segmental bands; pectus and ventral surface of abdomen brownish white; legs black-brown irrorated with white, the tarsi ringed with white. Fore wing black-brown irrorated with grey-white; a grey-white antemedial band traversed by a black line which is rather oblique to median nervure; a faint blackish discoidal spot; subterminal line indistinct, grey-white, excurved at middle. Hind wing whitish suffused with brown, especially on the veins, costal and terminal area; a dark terminal line; cilia white with a dark line near base.

W. AUSTRALIA, Waroona (*Berthoud*), 1 ♀ type. *Exp.* 18 mm.

Auchmera homographis, sp. n.

♀. Head, thorax, and abdomen whitish tinged with reddish brown, the antennæ fuscous ringed with whitish; pectus and legs white mixed with some brown, the tarsi ringed with brown; ventral surface of abdomen ochreous-white. Fore wing grey-white mixed with pale reddish brown and some blackish; antemedial line whitish with slight blackish points on its outer side at the veins and a patch of blackish irroration before it at inner margin, oblique, sinuous; subterminal line whitish defined on inner side by blackish, very slightly excurved at middle; some blackish scales on termen and a brown line through the cilia; hind wing semihyaline white tinged with brown; a dark terminal line, cilia white.

ALGERIA, Batna (*Eaton*), 1 ♀ type. *Exp.* 20 mm.

Genus TRICHORACHIA, nov.

Type, *T. leonina*.

Proboscis fully developed; palpi upturned, the second joint reaching to vertex of head and rather broadly scaled in front, the third rather long and thickly scaled; maxillary palpi slightly dilated with scales; frons smooth; eyes large, round; antennæ of male somewhat laminate and minutely ciliated; tibiæ slightly fringed with hair. Fore wing rather narrow, the costa slightly arched, the apex rounded, the termen obliquely curved; vein 2 from well before angle of cell, oblique; 3 from before angle; 4–5 stalked, not in line with the median nervure; 6 from upper angle; 8–9 stalked; 10–11 from cell; the male on underside with oblique ridge of long upturned hair from origin of vein 8 to vein 6 before termen. Hind wing with the cell about one-third length of wing; vein 2 from just before angle of cell; 3 and 5 strongly stalked, 4 absent; 6–7 stalked; 8 not anastomosing with 7.

Trichorachia leonina, sp. n.

♂. Head and thorax red-brown mixed with some whitish; abdomen whitish suffused with rufous. Fore wing red-brown irrorated with whitish; an obliquely curved whitish antemedial line; an oblique whitish subterminial line; a dark terminal line and white line at base of cilia. Hind wing semihyaline white, the costal and terminal areas slightly tinged with ochreous.

SIERRA LEONE (*Clements*), 4 ♂; S. RHODESIA, Umvuma (*Janse*), 1 ♂.

Genus HARRARIA, nov.

Type, *H. rufipicta*.

Proboscis fully developed; palpi with the second joint obliquely porrect, extending about twice the length of head, the third short, downturned; maxillary palpi of male brush-like, in a fold of the labial palpi; frons with horizontally flattened corneous plate covered by a tuft of hair; eyes large, round; antennæ of male minutely ciliated with a slight sinus at base of shaft containing minute scale-teeth; tibiæ smoothly scaled; abdomen with slight crests on two basal segments. Fore wing narrow, the apex rounded, the termen obliquely curved; vein 2 from towards angle of cell, curved; 3 from just before angle; 4–5 from angle, in line with the median nervure; 6 from upper angle; 8–9 stalked; 10–11 from cell. Hind wing with the cell about half the length of wing; vein 2 from angle of cell; 3 and 5 strongly stalked, 4 absent; the discocellulars obliquely curved; 6–7 stalked; 8 not anastomosing with 7.

Harraria rufipicta, sp. n.

♂. Head and thorax greyish suffused with rufous, the antennæ brown, greyish above, the palpi brownish grey, the third joint darker brown; abdomen greyish tinged with fulvous; pectus, legs, and ventral surface of abdomen brownish white. Fore wings brownish grey, the submedian interspace suffused with rufous to the antemedial line which is whitish, oblique, and slightly sinuous, a patch of rufous and black scales on its inner side at inner margin, and blackish points on its outer side below costa and at median nervure and vein 1; a small rufous discoidal spot with some blackish scales on it, crossed by a rufous streak from before end of cell to the subterminal line, which is whitish defined on inner side by black-brown, oblique towards costa and slightly angled inwards at discal and submedian folds; the terminal area suffused with rufous and with some black-brown scales towards termen; cilia tinged with rufous.

Hind wing semihyaline whitish tinged with rufous ; a brown terminal line; cilia whitish with a brown line near base.

Abyssinia, Harrar (*Degen*), 1 ♂ type. *Exp.* 22 mm.

Genus Homœograpta, nov.

Type, *H. spectrifasciella.*

Proboscis fully developed; palpi of male upturned, with the second joint reaching to rather above vertex of head, moderately scaled in front and hollowed out to receive the brush-like maxillary palpi, the third short and thickly scaled; frons with large thickly scaled conical prominence; eyes large, round; antennæ of male almost simple; tibiæ smoothly scaled. Fore wing narrow, the apex rounded, the termen obliquely curved ; veins 2 and 3 curved, from close to angle of cell ; 4–5 from angle ; 6 from upper angle ; 8–9 stalked ; 10–11 from cell. Hind wing with the cell about half the length of wing ; vein 2 from angle of cell ; 3 and 5 on a long stalk, 4 absent; the discocellulars obliquely curved ; 6–7 shortly stalked ; 8 closely approximated to 7 to about three-fourths length of wing.

Homœograpta spectrifasciella.

Staudingeria spectrifasciella, Rag. Ann. Soc. Ent. Fr. 1887, p. 250; id. Rom. Mém. viii. p. 140, pl. 28. f. 14 ; Staud. Cat. Lep. pal. ii. p. 21.

W. Turkestan.

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Genus Œdilepia, nov.

Type, *Œ. striginervella.*

Proboscis fully developed; palpi upturned, the second joint reaching to about vertex of head, moderately scaled, in male typically hollowed out to receive the large brush-like maxillary palpi, the third short, thickly scaled; frons smooth, with large tuft of scales above ; eyes large, round ; antennæ of male typically with short branches on outer side towards base, then serrate to about two-thirds length, ciliated on inner side, a small scale-tooth on shaft above towards base, the basal joint long ; the metathorax with paired tufts of scales at sides ; hind tibiæ with slight tufts of hair above at base and extremity ; abdomen with minute flattened dorsal crest at base. Fore wing narrow, the apex rounded, the termen evenly curved; vein 2 from towards angle of cell, curved ; 3 from just before angle ; 4–5 closely approximated for some distance, not in line with the median nervure; 6 from upper angle; 8–9 stalked; 10–11 from cell; the upper side with oblique antemedial and erect medial series of bosses of raised scales except towards costa. Hind wing with the cell about half the length of wing; its lower extremity produced; vein 2 from before angle of cell; 3 approximated for some distance to 4–5 which are strongly stalked; the discocellulars obliquely curved; 6–7 shortly stalked; 8 not anastomosing with 7.

Sect. I.—Palpi of male with the second joint hollowed out to receive the brush-like maxillary palpi; antennæ with short branches on outer side towards base, then serrate to two-thirds length, ciliated on inner side, a small scale-tooth on shaft above towards base.

Œdilepia striginervella.

Nephopteryx striginervella, Hmpsn. J. Bomb. Nat. Hist. Soc. xv. p. 23 (1903).

CEYLON.

Sect. II.—Maxillary palpi of male filiform, the palpi with large tuft of scales on second joint at extremity behind; antennæ somewhat laminate and almost simple, a sinus at base of shaft containing a double ridge of scales; hind wing on underside with slight streaks of androconia on subcostal and median nervures to end of cell.

Œdilepia stictoglaucella, sp. n.

♀. Head and thorax white slightly mixed with brown, the palpi with the second and third joints blackish at base; abdomen white with brownish bands; tarsi black-brown ringed with white. Fore wing white irrorated with dark brown, obliquely-placed antemedial bosses of raised blackish scales in lower part of cell and above and below vein 1; a white medial line, strongly excurved below costa, then oblique, bosses of raised black scales before it in lower part of cell and above vein 1; a blackish discoidal bar with grey striga in centre, a boss of raised white and dark scales before it, and another in submedian interspace; subterminal line white, interrupted and with short black streaks before and beyond it, strongly bent inwards below costa and with longer streaks before and beyond it, then oblique to vein 5, then dentate, strongly bent inwards in submedian interspace and acutely angled outwards above inner margin, a black mark beyond it on costa; a terminal series of small black spots; cilia white tinged with brown. Hind wing semi-hyaline white, the veins, costal area, and termen tinged with brown; a dark terminal line and brown line near base of cilia.

NATAL, Umkomaas, in Coll. Janse; CAPE COLONY, Annshaw (*Miss F. Barrett*), 3 ♀ type. *Exp.* 24–26 mm.

Genus ASEMEIA, nov.

Type, *A. aprepia.*

Proboscis fully developed; palpi with the second joint obliquely upturned to about vertex of head, rather curved forward at extremity and moderately scaled, the third porrect, short and thickly scaled; maxillary palpi filiform; frons smooth; eyes large, round; antennæ of female somewhat laminate and almost simple; tibiæ smoothly scaled. Fore wing narrow, the apex rounded, the termen evenly curved; vein 2 from towards angle of cell, curved; 3 from just before angle; 4–5 from a point, in line with the median nervure; 6 from upper angle; 8, 9, 10 stalked; 11 from cell. Hing wing with the cell about one-third length of wing; vein 2 from angle of cell; 3 strongly stalked with 4–5; the discocellulars oblique; 6–7 strongly stalked; 8 anastomosing with 7.

Asemeia aprepia, sp. n.

♀. Head and thorax pale ochreous-brown; abdomen fulvous-yellow, the basal segment pale ochreous-brown; pectus and legs white mixed with pale ochreous-brown. Fore wing pale ochreous-brown mixed with whitish and without markings, except a slightly darker discoidal striga. Hind wing whitish suffused with pale ochreous-brown.

CEYLON, Puttalam (*Pole*), 1 ♀ type. *Exp.* 16 mm.

Genus HOMODIGMA, nov.

Type, *H. geera.*

Proboscis fully developed; palpi upturned, smoothly scaled, the second joint reaching to vertex of head, the third moderate; maxillary palpi triangularly dilated with scales; frons smooth, with a tuft of scales; eyes large, round; antennæ of female somewhat laminate and almost simple; hind tibiæ with a tuft of long hair above from base and fringe of hair towards extremity. Fore wing narrow, the apex rounded, the termen evenly curved; vein 2 from well before angle of cell, oblique; 3 from just before angle; 4–5 from a point, not in line with the median nervure;

6 from upper angle ; 10 strongly stalked with 8–9 ; 11 from cell. Hind wing with the cell about one-third length of wing ; vein 2 from angle of cell ; 3 strongly stalked with 4–5 ; the discocellulars oblique ; 6–7 stalked ; 8 not anastomosing with 7.

Homodigma geera, sp. n.

♀. Head and thorax red-brown, the frons and palpi whitish suffused with red-brown, the latter with faint red-brown rings near extremity of second joint and at middle of third ; abdomen whitish suffused with red-brown ; pectus and legs grey mixed with red-brown, the hind tibiæ with a black band towards extremity. Fore wing red-brown mixed with grey ; medial line represented by an oblique blackish striga from costa, points on subcostal and median nervures, and a whitish mark in submedian interspace ; subterminal line whitish defined on inner side by dark scales, bent outwards below discal fold, then oblique ; a black terminal line except towards apex and tornus, and ochreous line at base of cilia. Hind wing semihyaline whitish tinged with red-brown ; a darker terminal line and white line at base of cilia, followed by a brown line.

CEYLON (*Alston*) 1 ♀, Peradeniya 1 ♀ type. *Exp.* 20–24 mm.

Genus PROCUNEA, nov.

Type, *P. siderea.*

Proboscis fully developed ; palpi upturned, the second joint reaching to vertex of head, the first and second joints very broadly scaled in front, the third short and thickly scaled ; maxillary palpi long and broadly dilated with scales, porrect and lying between the labial palpi ; frons with very large tuft of scales above, flattened below and rounded above ; eyes large, round ; antennæ of male somewhat laminate and almost simple, a large double ridge of scales at base of shaft but no sinus, the basal joint dilated ; the vertex of head hollowed out and with a large fan of scales behind ; a tuft of hair below base of fore wing, fore femora with large tuft of hair above, the hind tibiæ with tufts of hair above at base and extremity ; abdomen with flattened crests on two basal segments, the second segment rather hollowed out subdorsally. Fore wing narrow, the costa arched, the apex rounded, the termen evenly curved ; the cell narrow and the median nervure slightly curved upwards ; vein 2 from near angle of cell, curved ; 3 from angle ; 4–5 almost from a point ; 6 from upper angle ; 8–9 stalked ; 10–11 from cell.

Hind wing with the cell about one-third length of wing; vein 2 from angle of cell; 3 strongly stalked with 4–5; the discocellulars obliquely curved; 6–7 stalked; 8 not anastomosing with 7; the male with the costa strongly arched, with an elongate patch of rough scales below its basal half on upper side, and vein 8 rather sinuous and not approximated to the cell, and vein 7 from near base to about three-fourths of wing.

Procunea siderea, sp. n.

♂. Head, thorax, and abdomen grey tinged with iron-brown; pectus, legs, and ventral surface of abdomen whitish slightly tinged with brown. Fore wing grey, the costal half irrorated with dark brown, the inner half suffused with iron-brown; a medial black point on vein 1; an obliquely curved postmedial series of short black streaks on veins 6 to 1; a terminal series of black points in the interspaces between veins 8 and 2, with a few black scales beyond them on the cilia. Hind wing semihyaline white, the inner one tinged with ochreous; a fine brown terminal line and line near base of cilia.

QUEENSLAND, Townsville (*Dodd*), 1 ♂ type. *Exp.* 28 mm.

Genus PSAMMIA, nov.

Type, *P. flavipicta*.

Proboscis rather small and slender; palpi downcurved, extending about two and a half times length of head and moderately scaled; maxillary palpi filiform; frons with large rounded prominence with corneous plate below it; eyes large, round; antennæ of male with long cilia; tibiæ smoothly scaled. Fore wing long and narrow, the apex rounded, the termen evenly curved; vein 3 from towards angle of cell, curved; 3 from before angle; 4–5 from a point, not in line with the median nervure; 6 from upper angle; 8–9 stalked; 10–11 from cell. Hind wing with the cell about one-third length of wing; vein 2 from angle of cell; 3 strongly stalked with 4–5; the discocellulars angled; 6–7 shortly stalked; 8 not anastomosing with 7.

Psammia flavipicta, sp. n.

♂. Head and thorax ochreous-white with a few brown scales, the antennæ brownish, the frons with black points at sides; abdomen, pectus, and legs ochreous-white, the tarsi ringed with brown. Fore wing ochreous-white irrorated with black; antemedial line black defined on inner side by white and with a fulvous-yellow band before it below discal fold, oblique, waved, a diffused fulvous-yellow fascia beyond it in submedian interspace, and a small discoidal annulus; postmedial line formed by diffused black scales with an ill-defined white band on its outer side, very oblique from costa towards apex to lower angle of cell, then strongly angled outwards and again oblique to inner margin; a diffused black terminal line. Hind wing creamy white with a slight blackish terminal line except towards tornus.

U.S.A., Florida, 1 ♂ type. *Exp.* 24 mm.

Genus MELANASTIA, nov.

Type, *M. bicolor*.

Proboscis rather slender; palpi downcurved, in male extending about twice the length of head, the second joint hollowed out to receive the brush-like maxillary palpi and with tuft of scales above at extremity, the third moderate and thickly scaled, in female extending about three times length of head and smoothly scaled; frons smooth; eyes large, round; antennæ of male with the basal joint long and somewhat dilated, the shaft minutely serrate with a large sinus at base containing a double ridge of scales; tibiæ smoothly scaled. Fore wing narrow, the costa arched, the apex rounded, the termen evenly curved; vein 2 from well before angle of cell, oblique; 3 from near angle; 4–5 approximated for some distance, not in line with the median nervure; 6 from upper angle; 8–9 stalked; 10–11 from cell. Hind wing with the cell about half the length of wing; vein 2 from well before angle of cell; 3 approximated for a short distance to 4–5 which are strongly stalked; the discocellulars curved; 6–7 strongly stalked; 8 not anastomosing with 7.

Melanastia bicolor, sp. n.

Head, thorax, and abdomen glossy black-brown; tarsi ringed with white. Fore wing uniform glossy black-brown irrorated with a few white scales especially on inner area. Hind wing semihyaline white faintly tinged with brown; a brown terminal line and line near base of cilia.

S. NIGERIA, Yorubaland, Ogbomosa (*Sir G. Carter*), 1 ♂, 1 ♀ type; MASHONALAND, Salisbury (*Marshall*), 1 ♂. *Exp.* 20–24 mm.

Genus VELDTICOLA, nov.

Type, *V. striatella.*

Proboscis fully developed; palpi thickly scaled, the second joint upturned to about vertex of head and with slight tuft of scales behind at extremity, the third moderate, porrect; maxillary palpi somewhat dilated with scales; frons smooth; eyes large, round; antennæ of male somewhat laminate and almost simple, the basal joint long, the shaft with a sinus at base containing a double ridge of scales; hind tibiæ with slight tufts of hair above at base and extremity; abdomen with small flattened dorsal crests on the two basal segments. Fore wing narrow, the apex rounded, the termen evenly curved; vein 2 from well before angle of cell, oblique; 3 from near angle; 4–5 from angle, approximated for some distance and almost in line with the median nervure; 6 from upper angle; 8–9 stalked; 10–11 from cell. Hind wing with the cell about half the length of wing; vein 2 from well before angle of cell; 3 from angle, approximated for some distance to 4–5 which are strongly stalked; the discocellulars curved; 6–7 shortly stalked; 8 anastomosing with 7. The male on underside with some black androconia on costal area of both wings to beyond middle.

Veldticola persinuella, sp. n.

♀. Head and thorax grey-white tinged with brown, the palpi whitish with an oblique brown band towards extremity of second joint; abdomen dark brown suffused with grey; pectus and ventral surface of abdomen whitish tinged with rufous, the legs whitish tinged with grey-brown. Fore wing pale brownish grey, the costal area, the area beyond the cell, and the terminal area whiter; a dark brown antemedial mark on costa and oblique black striga from costa; a black point in middle of cell with black streak beyond it in discal fold, with white spots above and below it; the veins on costal area towards apex white defined on outer side by slight black streaks; the postmedial area with black streaks on veins 4 to 1 and on inner margin, and short streaks on veins 7 to 5 before the subterminal line which is black defined on outer side by white, strongly excurved between veins 5 and 2, then strongly angled inwards at submedian fold and outwards at vein 1; a black terminal line; cilia with fine white lines near base and tips. Hind wing semihyaline white with a faint brown tinge; a brown terminal line; cilia white with a brown line near base.

TRANSVAAL, White R. (*Cooke*), 1 ♀ type. *Exp.* 26 mill.

Veldticola striatella, sp. n.

Head and thorax purplish grey, the head with some black scales, the tegulæ, patagia, and dorsum of thorax with black streaks, the antennæ black, the palpi blackish, whitish above; abdomen rufous with the basal crests grey; pectus, legs, and ventral surface of abdomen white and blackish. Fore wing purplish grey, the veins streaked with black to the subterminal line and black streaks in discal and submedian folds to end of cell, a white streak above median nervure; antemedial line represented by a white line to median nervure angled outwards below costa and a diffused black mark defined on inner side by white above inner margin; subterminal line white defined on each side by black, slightly excurved from vein 7 to submedian fold; a black terminal line and fine yellowish line at base of cilia. Hind wing semihyaline white with a faint brownish tinge; a brown terminal line; cilia pure white with a fine yellowish line at base followed by a brown line.

The male on underside with black androconia on costal area of both wings to beyond middle.

Transvaal (*Pead*) 1 ♂ type, Pretoria (*Janse*) 1 ♀. *Exp.* 24 mm.

Veldticola nebulosella, sp. n.

♀. Head and thorax grey-white, the tegulæ with some black scales, the patagia with black streaks, the antennæ black, the palpi white and black with a black patch near extremity of second joint; abdomen pale rufous with some dark scales, the crests on basal segment grey; pectus and legs black mixed with white, the tarsi tinged with white. Fore wing grey-white thickly irrorated and clouded with dark brown; an antemedial black shade with black streaks on it at subcostal and median nervures and a diffused black patch at inner margin; a slight white streak above median nervure except towards base; black spots defined by white except on inner side at extremities of subcostal and median nervures and a black spot with white before and beyond it at middle of vein 1; subterminal line white defined on each side by diffused black, rather indistinct, excurved from vein 7 to submedian fold; a terminal series of ill-defined black points; cilia with a fine black line near tips. Hind wing semihyaline white, the costal area tinged with brown; a brown terminal line and line near base of cilia.

Transvaal, Pretoria (*Janse*), 1 ♀ type. *Exp.* 26 mm.

Veldticola irrorella, sp. n.

♀. Head, thorax, and abdomen pale rufous irrorated with black, the antennæ pale red-brown; pectus and ventral surface of abdomen white tinged with rufous. Fore wing pale rufous thickly irrorated with black; traces of a pale antemedial line, slightly excurved between discal and submedian folds; a terminal series of prominent black points. Hind wing semihyaline white with a faint red-brown tinge; a brown terminal line and line near base of cilia.

TRANSVAAL, White R. (*Cooke*), 1 ♀ type. *Exp.* 28 mm.

Veldticola macra, sp. n.

♀. Head and thorax grey tinged with red-brown and slightly irrorated with black, the antennæ slightly tinged with black, the palpi with the extremity of second joint and the third joint darker; abdomen grey tinged with red-brown; pectus, legs, and ventral surface of abdomen grey tinged with red-brown and irrorated with black. Fore wing grey rather sparsely irrorated with black, the cell and area just beyond it whiter, the inner and terminal areas tinged with red-brown; antemedial line double, blackish filled in with whitish, rather oblique to submedian fold and angled inwards at vein 1; a black discoidal bar; subterminal line double, blackish filled in with whitish, oblique to discal fold and excurved at middle and vein 1; a rather punctiform black terminal line from just below apex to vein 2, and a whitish line at base of cilia. Hind wing whitish tinged with red-brown, a dark terminal line and line near base of cilia.

BR. E. AFRICA, Kinjabe (*Betton*), 1 ♀ type. *Exp.* 32 mm.

Veldticola megista, sp. n.

Head and thorax fuscous-brown mixed with pale bluish grey, the antennæ dark brown, the basal joint above and ridge of scales in male whitish; abdomen whitish and fuscous-brown with pale red-brown segmental bands; pectus, legs, and ventral surface of abdomen fuscous-brown and white, the tarsi blackish tinged with white. Fore wing bluish white tinged with brown and irrorated with black. Antemedial line rather diffused black-brown defined on inner side by white, oblique, angled outwards at discal and submedian folds and inwards at vein 1; two large black-brown discoidal points; subterminal line white defined on inner side by black-brown and less distinctly on outer, oblique to discal fold where it is angled inwards, angled outwards at middle, then oblique and dentate; a terminal series of black points. Hind wing semihyaline white, the veins of terminal half tinged with brown, the apical area suffused with brown; a blackish terminal line; cilia with a fuscous line near base and tinged with fuscous at tips.

MASHONALAND, Umtali (*Janse*), 1 ♂, 2 ♀ type. *Exp.* 34–42 mm.

Genus EMMERITA, nov.

Type, *E. mirandella.*

Proboscis fully developed; palpi upturned, broadly scaled, the second joint reaching to about middle of frons, the third short; maxillary palpi dilated with scales, in male the palpi hollowed out to receive the large brush-like maxillary palpi; frons smooth; eyes large, round; antennæ of male somewhat laminate and almost simple, the shaft with sinus at base containing a double ridge of scales; hind tibiæ with small tufts of hair above at base and extremity; abdomen with small flattened dorsal crests on two basal segments. Fore wing rather narrow, the costa arched, the apex rounded, the termen evenly curved; vein 2 from well before angle of cell, oblique; 3 from just before angle; 4–5 approximated for some distance, not in line with the median nervure; 6 from upper angle; 8, 9, 10 stalked; 11 from cell. Hind wing with the cell about half the length of wing, the lower angle produced; vein 2 from near angle of cell; 3 approximated for some distance to 4–5 which are strongly stalked; the discocellulars curved; 6–7 shortly stalked; 8 not anastomosing with 7.

Emmerita mirandella.

Meroptera mirandella, Rag. Rom. Mém. vii. p. 313, pl. 47. f. 4 (1893); Dyar, Cat. Lep. N. Am. p. 423.

U.S.A., Colorado.

Genus STYPHLORACHIS, nov.

Type, *S. mesophæa.*

Proboscis fully developed; palpi upturned, the second joint hardly reaching to vertex of head and rather broadly scaled in front, the third rather long and thickly scaled; maxillary palpi filiform; frons smooth; eyes large, round; antennæ somewhat laminate and almost simple; tibiæ smoothly scaled. Fore wing rather narrow, the apex rounded, the termen evenly curved; vein 2 from towards angle of cell, curved, 3 from just before angle; 4–5 from a point; 6 from upper angle; 8–9 stalked; 10–11 from cell; the upper side with an antemedial ridge of raised scales except towards costa. Hind wing with the cell about one-third length of wing; vein 2 from before angle of cell; 3 from angle; 4–5 strongly stalked; the discocellulars curved; 6–7 shortly stalked; 8 anastomosing with 7.

Styphlorachis mesophæa, sp. n.

♀. Head and thorax dark olive-brown mixed with some whitish, the antennæ dark brown, the palpi dark brown mixed with white; abdomen pale olive-brown with whitish segmental lines; pectus and legs white mixed with blackish, the tarsi black ringed with white. Fore wing olive-brown suffused with dark brown; an oblique triangular white patch irrorated with black from costa to inner margin before the broad antemedial ridge of silvery blackish scales which is followed by a conical patch of cupreous-red and olive before the dark antemedial line which is oblique to submedial fold and slightly incurved at vein 1; the medial costal area blackish; an obliquely curved blackish discoidal bar with an oblique triangular white patch thickly irrorated with blackish from postmedial part of costa to its outer side; subterminal line whitish defined on each side by diffused blackish, incurved to vein 5, then very slightly waved and incurved below vein 3; a terminal series of black points and white line at base of cilia. Hind wing white tinged with brown especially on the veins and costal area; a brown terminal line and line near base of cilia.

Br. C. Africa, Lake Nyasa (*de Jersey*), 1 ♀; Transvaal, White R. (*Cooke*) 1 ♀, Barberton (*Janse*) 4 ♀ type. *Exp.* 18 mm.

Genus Myelodes, nov.

Type, *M. jansei.*

Proboscis fully developed; palpi downcurved, extending about twice the length of head and thickly scaled; maxillary palpi dilated with scales at extremity; frons smooth; eyes large, round; antennæ of female laminate and almost simple; hind tibiæ fringed with hair above. Fore wing narrow, the apex rounded, the termen evenly curved; vein 2 from towards angle of cell; 3 from before angle; 4–5 stalked; 6 from well below upper angle; 8–9 stalked; 10–11 from cell. Hind wing with the cell more than half the length of wing; vein 2 from long before angle of cell; 3 from angle; 4–5 strongly stalked: the discocellular curved; 6–7 from upper angle; 8 not anastomosing with 7.

Sect. I.—Fore wing with veins 4–5 strongly stalked.

Myelodes flavimargo, sp. n.

♀. Head and throat silvery white, the antennæ tinged with fuscous, the palpi orange-yellow; abdomen orange-yellow, the basal segment white; pectus, legs, and ventral surface of abdomen white tinged with yellow, the fore legs streaked with black above, the mid-femora black above at extremity. Fore wing silvery white, the costa, termen, and cilia yellow, the costal edge black towards base; small antemedial black spots on median nervure and vein 1, two discoidal spots and a curved subterminal series; a terminal series of black points except towards apex and tornus. Hind wing pale yellow. Underside of fore wing yellow suffused with black except on inner and terminal areas.

TRANSVAAL, Pretoria (*Janse*), 2 ♀ type; BASUTOLAND, Masite (*Weigall*), 1 ♀. *Exp.* 22 mm.

Sect. II.—Fore wing with veins 4–5 very shortly stalked.

Myelodes jansei, sp. n.

♀. Head white with a black bar above the frons, the antennæ black, barred with white above, the palpi with the second and third joints black above, except at tips, the maxillary palpi black, white at tips; tegulæ golden-yellow, with black spots at base; thorax slate-grey with some black on prothorax; abdomen golden-yellow; pectus yellow, white in front; legs white, the fore legs black above, the mid-femora and base of tibiæ black above, the hind legs black mixed with white, the tibiæ fringed with yellow hair above, the spurs and tarsi black, the latter ringed with white. Fore wing silvery white to median nervure and vein 5, the costal edge black, expanding with a patch at base; the inner half o wing slate-grey, extending on terminal area to near apex; a small black spot below base of cell; antemedial spots in the cell and on median nervure and vein 1, the spot in the cell nearer the base; two discoidal spots, a curved subterminal series to vein 2 and a slight spot on vein 1, a terminal series. Hind wing golden-yellow; a terminal fuscous line to vein 4. Underside of fore wing fuscous, some white below costa towards base and some yellow in upper part of cell except towards base, a diffused black postmedial spot on costa with some whitish suffusion before and beyond it.

S. Rhodesia, Umtali (*Janse*), 1 ♀ type. *Exp.* 46 mm.

Genus Meyrickialis, nom. nov.

	Type.
Meyrickiella, Hmpsn. Rom. Mém. viii. p. 86 (1901), nec Berg, 1898	*homosema.*

Proboscis fully developed; palpi upturned, the second joint reaching to vertex of head and moderately scaled, the third short and thickly scaled; maxillary palpi filiform; frons rounded and thickly scaled; eyes large, round; antennæ of male somewhat laminate and almost simple, the shaft with a sinus at base containing a large ridge of scales; fore and mid tibiæ smoothly scaled, the hind tibiæ with a small tuft of hair above at extremity. Fore wing narrow, the costa slightly arched, the apex rounded, the termen evenly curved; vein 2 from towards angle of cell, curved; 3 from just before angle; 4–5 strongly stalked; 6 from upper angle; 8–9 stalked; 10–11 from cell. Hind wing with the cell about one-fourth length of wing; vein 2 from well before angle of cell; 3 and 5 from angle, 4 absent; the discocellulars erect; 6–7 stalked; 8 anastomosing with 7.

Meyrickialis homosema.

Hypophana homosema, Meyr. Trans. Ent. Soc. 1887, p. 264; Rag. Rom. Mém. viii. p. 86, pl. 26. f. 15.

W. Australia; N.S. Wales; S. Australia.

Genus Anousterunia, nom. nov.

	Type.
Pogonophorus, Saub. Verh. Ver. Naturw. Unterh. Hamb. x. p. 63 (1899), nec Latr. Coll. 1802	*tancrei.*
Pogonotrophus, Saub. Verh. Ver. Naturw. Unterh. Hamb. x., Corrig. (1899), nec *Pogonatropha*, Zell. Lep. (1852)	*tancrei.*

Proboscis fully developed; palpi porrect, in male extending about one and a half times length of head, in female about the length of head, almost hidden by long hair; maxillary palpi minute; head hairy, the frons without prominence; eyes rather small in male, small in female, round; antennæ of male typically with fasciculate cilia; tibiæ fringed with hair above. Fore wing narrow, the apex rounded, the termen evenly curved; vein 2 from towards angle of cell; 3, 4, 5 separate; 6 from upper angle; 8–9 stalked; 10–11 from cell. Hind wing with the cell about half the length of wing; vein 2 from well before angle of cell; 3 and 5 from angle, 4 absent; the discocellulars angled; 6–7 from upper angle or shortly stalked; 8 typically anastomosing with 7.

Sect. I.—Antennæ of male with fasciculate cilia; hind wing with veins 6–7 from upper angle of cell, 8 anastomosing with 7.

Anousterunia tancrei.

Pogonophorus tancrei, Sauber, Verh. Ver. Naturw. Unterh. Hamb. x. p. 63 (1899); Staud. Cat. Lep. pal. ii. p. 25.

W. TURKESTAN.

Sect. II.—Antennæ of male laminate and minutely ciliated; hind wing with veins 6–7 shortly stalked, 8 not anastomosing with 7.

Anousterunia alticola, sp. n.

♂. Head and thorax black-brown with a slight rufous tinge; abdomen black-brown, the anal tuft grey-white; pectus and legs black-brown, the tarsi tinged with grey-white. Fore wing grey-white mixed with very dark red-brown, the discal fold beyond the cell and submedian fold with obscure rufous streaks; antemedial line strong, white defined on outer side by rather diffused black, oblique and slightly excurved; an oblique black discoidal bar; subterminal line white strongly defined on inner side by black, rather oblique and slightly excurved at middle; a terminal series of rather diffused black points; cilia whitish at base, pale red-brown at tips. Hind wing blackish tinged with grey, the costa to near apex and the cilia except at base whiter. Underside greyish suffused with fuscous, the terminal area of fore wing and the apical area of hind wing greyer; fore wing with oblique black postmedial line slightly excurved at middle.

KASHMIR, Rupshu, 17,500 feet (*Avinoff*), 1 ♂ type. *Exp.* 20 mm.

IV.—*New* Derbidæ *from Sierra Leone* (Homoptera Fulgoroidea).

By F. Muir.

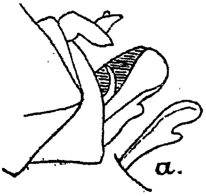
The species mentioned below were submitted to me, along with others, for identification by the Imperial Bureau of Entomology. The types will be placed in the collection of the British Museum (Natural History).

Cedusa nigripes, sp. n. (Fig. 1.)

Male.—Length 1·8 mm.; tegmen 2·5 mm.

Shoulder-keels not very large; subantennal plate longer than wide; length of frons twice the width, no median carina; width of vertex at base twice the length, base wider than apex. *M* with five apical veins, viz., 1, 1 *a*, 2, 3, 4; forking of *Sc*+*R* and *Cu* about level; cross-veins near nodal line, apical cross-veins subparallel to apical margin.

Lateral and ventral margins of pygofer entire, slightly curved; anal segment small, apex rounded; genital styles small, apex round, a curved spine near base on dorsal margin, inner margin produced into a round process about the middle.



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Cedusa nigripes, sp. n.

Lateral view of male genitalia; *a*, ventral view of left genital style.

Head and thorax stramineous; middle of clypeus and frons fuscous, thorax darker; labium dark fuscous; front legs dark fuscous, hind legs with the femora and first two tarsi stramineous, rest fuscous; abdomen reddish brown. Tegmina hyaline, slightly fuscous or dirty stramineous, veins darker; wings hyaline with brown veins.

Female.—Length 1·8 mm.; tegmen 3 mm.

Similar to the male in build and colour. Pregenital plate angularly produced from sides to middle.

Hab. Sierra Leone, Kailahun, "ex Piasaara" (*E. Hargreaves*, May 1928), described from four males and four females.

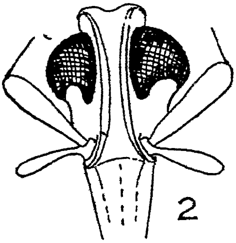
Phenice bicornis, sp. n. (Figs. 2, 3.)

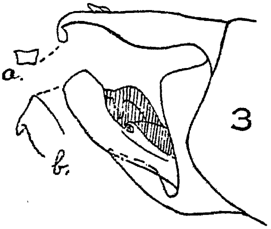
Male.—Length 2·9 mm.; tegmen 5·3 mm.

This species differs from all the others of the genus in having the basal segment of the antenna produced into a long, narrow, flattish process. Antennæ about as long as the frons, the process from the basal segment not so long as the second segment. Carinæ on clypeus obscure. Basal *Ms* furcate at the spot where *M–Cu* cross-vein joins it.

The anal segment truncate at apex, which is curved ventrad; medio-ventral process large, lanceolate; genital styles long, inner margins entire, slightly curved, outer margin produced into a small curved spine slightly before middle, apex truncate, the inner corner slightly produced.

Stramineous; slightly darker over frons and antennæ. Tegmina hyaline with light fuscous marks, over base of clavus extending over base of radial and subcostal and apical half of costal, another mark from apex of clavus to base of *Ms* 1; a darker mark over cross-vein of *Cu* extending into membrane, the cross-veins of *Ms* and *R–M* dark, veins otherwise light. Wings hyaline, slightly fuscous.





Phenice bicornis, sp. n.

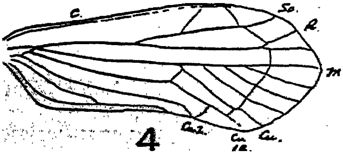
Fig. 2.—Front view of head.
Fig. 3.—Lateral view of male genitalia; *a*, apex of anal segment; *b*, apex of genital style.

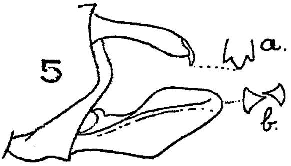
Female.—Length 3·7 mm.; tegmen 6·9 mm.

Antennæ slightly shorter than in male, and the process on the base also shorter. The ovipositor longer than is general in Derbidæ. Pregenital plate with hind margin angularly produced from middle to sides.

Colour similar to male, but with the dark marks over *Cu* and *M* cross-veins darker.

Hab. Njala, Sierra Leone; "at light" (*E. Hargreaves*, Dec. 1928; August, December, 1928). Two males and one female.





Patara hargreavesi, sp. n.

Fig. 4.—Right tegmen.
Fig. 5.—Lateral view of male genitalia; *a*, apex of anal segment; *b*, apices of genital styles.

Patara hargreavesi, sp. n. (Figs. 4, 5.)

Male.—Length 1·9 mm.; tegmen 2·8 mm.

This differs from the typical species of the genus in having a small subquadrate subantennal plate situate more behind than beneath the antenna. The venation of the tegmen is similar to that of *Patara pattersoni* *, the only other species of the genus so far reported from Africa. They both differ from the type, *P. guttata*, in the *Cu* and in having an extra *Ms*, but I consider that they must both come into the genus.

Antennæ not as long as the frons, thick and wide; a small quadrate plate arising from the head behind the antenna, the distal margin bearing hairs. Vertex triangular, small; frons narrow.

Anal segment long, narrow, the apex produced into three small processes, the middle one curved downward. Genital styles long, fairly narrow, widest about middle, where the inner margin is angular, apices pointed and curved inward.

Shiny black; clypeus and legs yellow. Tegmina and wings black with a reddish tinge; apical portion of costal margin reddish, a small light mark at the apices of each vein entering the apical margin.

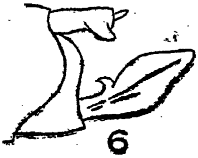
Female.—In size and colour similar to the male. Pregenital plate angularly produced from sides to middle, the two sides of the projecting angle slightly sinuate.

Hab. Kenema, Sierra Leone, on Oil Palm (*E. Hargreaves*, May 1928). Three males and three females.

Patara elæidis, sp. n. (Fig. 6.)

Male.—Length 1·5 mm.; tegmen 2·7 mm.

The antennæ about as long as the frons, broad and flat; no subantennal plate. The venation of tegmen similar to *P. guttata*, with three median sectors and only one branch to *Cu*.



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Patara elæidis, sp. n.
Lateral view of male genitalia.

Anal tube short, the apex produced into two small, conical processes, one on each side. Ventral margin of pygofer straight,

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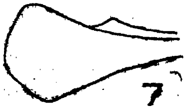
* This was omitted from the list published by the writer in Ann. & Mag. Nat. Hist. (10) i. p. 498. (Fig. 7.)



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Patara pattersoni.
Right genital style.

sides slightly curved; genital styles large, sublanceolate in outline, a small curved spine on dorsal margin near base.

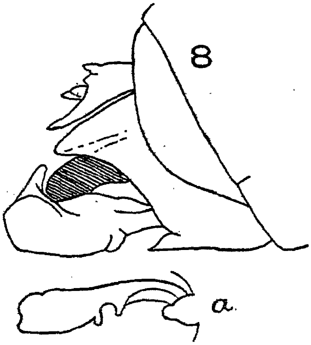
Frons, vertex, antennæ, and thorax yellow, the mesonotum darker; clypeus brown; front legs fuscous, middle and hind legs yellow; abdomen brown. Tegmina and wings fuscous with darker veins, the apical cells of tegmina lighter.

Hab. Sierra Leone, Kenema, on Oil Palm (*Elæis guineensis*, Jacq.) (*E. Hargreaves*, May 1928), one male.

There are three other specimens of this genus, representing two species, but as one is a damaged male and the others females I refrain from describing them.

Zoraida flavocostata, Dist.

This species was described from one female from Kola River, Portuguese East Africa. The specimens before me, which I place in this species, are from Sierra Leone, Njala (*E. Hargreaves*, Dec. 1927 and April 1928). I figure the male genitalia for comparison with the male from the type-locality.



Zoraida flavocostata ?, Dist.

Lateral view of male genitalia; *a*, ventral view of right genital style.

V.—*On the Multiple Tumours* (Lymphocystis) *of Plaice and Flounders.* By Emeritus Professor W. C. M'Intosh, M.D., D.Sc., LL.D., F.R.S., Gatty Marine Laboratory, University of St. Andrews.

[Plates I.–IV.]

This appears to be the affection mentioned by Dr. Lowe *, who frequently found it in flounders from the Ouse, Norfolk. He described it as a peculiar skin disease resembling epithelioma, large fungus growths cropping out over the whole body. The granulations are large and roe-like, consisting of large nucleated cells under the microscope.

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* Trans. Norfolk & Norwich Nat. Soc. 1873–74.

In the estuary of the Thames in 1883 many common flounders were thus attacked, besides being infected with *Caligi*. Like the haddocks suffering from gill-parasites and the green cod from *Caligi*, the fishes were generally out of condition.

In the third Annual Report of the Fishery Board for Scotland a note on these tumours affecting plaice at St. Andrews was made as follows:—

"The coloured surface of the fish was crowded with the small rounded tumours which resembled shot. They also occurred on the dorsal, ventral, pectoral, and caudal fins, and on the white surface. They are firmly fixed to the skin and give pain to the animal when interfered with. Moreover, they are vascular, free hæmorrhage occurring when they are injured. The isolated tumours range from 1·7 mm. to 1 mm. or less. The larger masses, when bisected, show a series of smaller areas, the whole being composed of multiple tumours [cells] mostly of the same size. When cut into in the fresh state, a whitish-creamy substance exudes, which, under a power of 400 diameters, is minutely granular, no distinct cell-elements being visible, though fine fibrillæ occur throughout the field as if the fluid were coagulable. In section [with a scalpel] the large tumours present a series of loculi, or spaces filled with the granular creamy fluid. Each chamber is cystic, presenting a firm hyaline wall of considerable thickness, within which is the granular contents. The stroma exterior to the hyaline coat is chiefly fibro-granular. Amongst the larger cysts are numerous smaller forms in course of development, the thick, translucent, hyaline wall being conspicuous" *.

Further examination † of a large multiple tumour projecting from the mouth of a flounder at St. Andrews showed that the fluid escaping from "the cut surface contained masses of small granular cells with distinct nuclei—these apparently being external to the encysted bodies forming the tumour, for the contents of the cysts were mainly granular."

Mr. George Sandeman ‡ subsequently examined these tumours at St. Andrews in 1893, observing that "an individual cyst is surrounded by a hyaline membrane, and is in close connection with the inner surface of the skin, which is always unbroken over it. The pearly-white sphere has no deep attachment, but lies in loose connective tissue. On pressure it bursts, and exudes a white, creamy, granular substance. . . Their enclosing membrane is hyaline and apparently structureless (pl. xvii. fig. 5) but for a radial striation in the inner layer, which gives it a resemblance to an egg-membrane with a *zona radiata*. . . It gives the staining reactions characteristic of yolk. . . The larger masses vary in size and shape, ranging from a tumour formed of two or three cysts to one an inch in length and half an inch in diameter. They may be broad at the base, but are usually narrow and projecting, sometimes even pedunculated." Between the cysts "is a varying amount of tissue, especially abundant near the base of the tumour, and consisting of fibrine and leucocytes, or of more or less advanced connective tissue, in one case of myxomatous tisssue. . . Young blood-vessels are usually present." The author thought they were unlike any known Protozoon or Protophyte, and mentions that the present writer once found *Diplozoon paradozicum* in one of the tumours.

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* S. F. B. Rep., Appendix, pp. 66–67, 1885.

† *Ibid.* No. 4, Appendix, p. 214, 1886.

‡ *Ibid.* for 1892 (1893), pt. 3, pp. 391–392, pl. xvii. figs. 1–7.

Dr. Woodcock *, in his careful description, observes, in regard to the cysts in the mesentery, that they are smaller than those outside—never exceeding 1 mm. in diameter. He supposes that when small they pass into the blood-vessels (capillaries) or lymph-channels from the gut, and then grow and encyst, "since in sections they are surrounded by a space." He found all the other viscera normal, so that the hosts did not appear to be seriously harmed. The cysts increase in size, but each remains a single cell, and he found no trace of cell-nuclei nor of cell-division. In his fig. 3 (pl. iii.) he gives a section, minutely covering the structurless investment with dots (never seen by the writer), the "capsule being surrounded by a layer of amœbocytes closely aggregated." Next comes a thick deeply-staining zone of a finely granular nature, the greater part of which gives the organ its character. "Centrally is a huge nucleus with a very thin nuclear membrane (from a cyst underneath the skin), and in it several nucleoli or karyosomes (since they retain the chromatic stain)." He considered these bodies unlike any known Protozoan, and he gave the name *Lymphocystis johnstonei* to them. He considered the tumours masses of cysts "with, of course, a little vascular connective tissue between and around them."

A. S. Awerinzew † procured a flounder with this sporozoan parasite in the mesentery, liver, ovary, as well as in the skin of the fish. The shape was generally ovoid, and it measured from 1 to 3 mm. in diameter. Out of 109 flounders 19 were affected, or 11 per cent. He alluded to the observations of Johnstone and Woodcock, pointing out that the Myxosporidian had the structure of the genus *Henneguya*, and thus he called Woodcock's form *H. johnstonei*. He found the youngest stage disk-shaped and measuring 0·060 to 0·090 mm., with an ectoplasmic tail (0·011 mm.), a cirrus of endoplasm, and a nucleus in the endoplasm. He goes into detail in regard to nuclei and nucleoli and their staining. The spore subsequently loses its tail. He did not allude to the structure of the wall of the tumour.

Two papers on the allied type, *Glugea*, by R. Weissenberg ‡ appeared in 1911 and 1913. In the first of these an account is given of an attack of the parasite on the central nervous system of *Lophius piscatorius*, and descriptions and figures closely approach those met with in the "multiple tumours" of plaice and flounders; yet, so far as the investigations have gone, none of the minute spores characteristic of *Glugea* have been encountered, though it is possible such early stages have been passed before the introduction of the parasite into the tumour. Moreover, Weissenberg shows that the capsule of the young *Glugea* is uniformly smooth amidst the nerve-cells; and he alludes to the budding chain (Sproskettten) of the schizont in the outer zone of the young *Glugea*.

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* Rep. xii. Lancashire Sea-Fisheries Lab. 1903, p. 63.

† "Leiter der mariner Biol. Murman," Zool. Anz. Bd. xxxi. no. 26, July 9, 1907 (with text-figs).

‡ Arch. f. Micros. Anat. Bd. lxxviii. p. 383, Taf. 18 & 19; *ibid.* lxxxii. p. 81, Taf. iv.-vii.

In the second paper he treats of the minute structures of *Glugea anomola*, Moniez, and of *G. hertwigi*, Weissenberg, the former occurring in the stickleback and the latter in the smelt. He deals exhaustively with both species, and figures the spores of *G. hertwigi*.

In a plaice procured in St. Andrew's Bay on the 15th August, 1895, a tumour nearly half an inch in diameter was situated behind the left eye and attached to the surface by a narrow pedicle (Pl. I. figs. 1 & 2), and thus had a certain amount of motion (Pl. I. figs. 1*a*–1*b*). Externally the surface was everywhere raised into the little eminences from the development of the egg-like cysts internally. On cutting through the tumour the entire contents consisted of these cysts, which varied in size from a quarter or less to 5 or 6 mm. In structure the surface of the section presented a fibro-granular matrix surrounding the cystic bodies, each of which had a structureless gelatinous investment of varying size, the interior being opaque and granular. On the left (pale) side of the fish (Pl. I. fig. 1 *a*) four flattened circular bodies were present, two towards the ventral and two near the dorsal margin and about half an inch from the dorsal fin. Each of these had the same cystic contents surrounded by the fibro-granular matrix. Further, besides the larger cysts in the sections of the fresh tissue, there were groups of much smaller forms, some of a nearly uniform size as well as others scattered singly, and such necessarily raised the question as to their origin. No sign of the development of these smaller bodies in the larger has ever been seen; nor can they arise from the fibro-granular matrix. In looking over the field of a preparation, a more distinctly cellular structure was once met within, the cyst, apparently of one size over the whole area; but such may have been due to preparation and pressure. No distinct gelatinous investment was seen in these cases. The appearance of this cyst resembled that figured by Weissenberg * in the upper part of the lower (right) cyst in fig. 7 (pl. xix.) in *Glugea lophii*, Doflein.

The field of a section of the entire turmour has the larger cysts occupying most of the space and surrounded by the general fibro-granular tissue, in which also groups of the smaller cysts and blood-vessels occur. The smaller (developing) cysts have no definite distribution, occurring throughout sometimes in groups of about 20 or more (Pl. II. fig. 14). This represents a group of a dozen small cysts nearly of equal size, a larger one being below. It is seldom that so considerable a series of almost uniform size is met with, irregular sizes (as in Pl. III. fig. 8) being more common. They may even reach the proximity of the investing layer, though such is generally the seat of the larger cysts. The latter show within the translucent gelatinous coat the "Plasmaschale" of Weissenberg, a mass of granules, whilst in the centre is a gelatinous area often with numerous processes or rays. Sometimes a median cyst (Pl. I. fig. 1) has a separate opaque granular area and a more translucent gelatinous area, as if the whole had undergone division, but such appears to be due to changes during the preparation, which also cause the gelatinous investment ("ectocyst"; "Plasmaschale," Weissenberg), often to shrink into a linear belt in section, and it is occasionally doubled or folded, each fold separated by a layer of granules (Pl. I. fig. 2). In some of the smaller cysts amœboid forms akin to those described by Awerinzew appear (Pl. I. figs. 4 & 4 *a*).

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* Arch. f. Micros. Anat. Bd. lxxxviii. 1911.

The tumour is highly vascular, and the field contains many blood-vessels—large and small—within some granular blood (corpuscles) or opaque bodies. Thus a minute larval form such as that described by Awerinzew might readily be introduced, and, indeed, in the smallest or first stage of the cyst is apparently present; once introduced, the larva, in the midst of rich nourishment, would seem simply to enlarge by compressing the surrounding stroma which alone forms its investment (figs. 5, 5 *a*, & 6), the former representing a blood-vessel containing a foreign body stained, the latter showing a pale investment. Occasionally the section of a vessel presents within its definite deeply-stained wall only a translucent, finely-reticulated substance; but, on searching its further course, corpuscles appear—thus demonstrating its nature. Such a vessel would contain a parasite of considerable size.

Some of the minute cysts show only an indefinite border to the cavity and a small circle of the structureless ectocyst (the gelatinous layer), within which are a few granules. In the most minute there is simply a black (stained) centre without an evident ectocyst, or perhaps only a trace of it at the circumference. Such is readily distinguished from a small blood-vessel by the well-defined wall of the latter—whereas the cystic wall is only part of the surrounding stroma (Pl. I. fig. 12 *a*). The occurrence of the smaller cysts in groups here and there may indicate occasional epochs of infection. The next stage to fig. 12 (Pl. I.) is the formation of the structureless ectocyst with the densely granular centre; the gelatinous substance in the early amœboid stage seems to be rapidly separated to form this investment.

The so-called fibro-granular matrix around and between the cysts appears to be formed of fine strands of the gelatinoid substance which plays so important a part in these parasites. The addition of the stain covers the field of these strands with multitudes of minute dark granules which vary in size and shape and seem to be due to the action of the stain on the constituents of the fibres themselves, being minute in much of the stroma, coarser and in rows in other parts. This tissue supports the numerous blood-vessels—large and small—throughout the tumour, and it is curious to note its divergent condition in the tumour on the tail.

When two adjoining cysts are cut obliquely, it is clearly shown that the narrow process of the stroma around and between them forms no special capsule for each cyst—a fact not in accordance with Dr. Woodcock's statement and figure * in those from the mesentery. Each cyst, he states, lies in a space "representing an enlarged capillary or lymph-chamber. It is surrounded by a layer of amœbocytes rather closely aggregated." In a more highly magnified section of the same cyst (fig. 6) he shows the external layer of a "thick, faintly-staining structureless membrane (*ect.*). Next comes a thick zone, more deeply staining, finely granular, the greater part of which presents a most unusual appearance and gives the organism its remarkable character. Centrally is what can only be a nucleus (N.). In each nucleus are several nucleoli, or rather karyosomes, since they retain chromatin stain. The nuclear membrane is very thin and irregular, and sometimes seems only a boundary between the nucleus and the inner limit of the critical region."

In studying the various sections † after staining with iron hæmatoxylin, the tumour presents externally a superficial series of circular areolæ (Pl. I. fig. 7 *a*), which vary a little in size in the stroma. These project in some cases as clear vesicles on the free edge, and give a character to the surface. The deeper part (Pl. I. fig. 7 *b*) of this thick layer is minutely cellular throughout, forming a compact investment. Within is a fibroid layer (Pl. I. fig. 7 *c*) profusely dotted with black points (stained), especially on its inner edge, so that it forms a nearly continuous black border against which the paler ground-tissue of the tumour rests—this, as a rule, intervening between the walls of the cysts and the inner cortical (dermal) layer. The subdermal fibroid layer might be mistaken for a muscular coat, but it is essentially different, being composed of fibrils (Pl. IV. fig. 18), which here and there have dilatations and contractions as if protoplasmic—which it really seems to be, though the continuous arrangement of the more or less separate fibrils is striking. The coat is, perhaps, less developed in this tumour than in that attached to the tail, as will subsequently be shown.

The cysts (Pl. I. figs. 2, 4, & 7 and Pl. II. figs. 13, 14, & 15) present diverse aspects in the sections, and the translucent, friable, gelatinous investment is much altered. In some the contents are deeply stained with large black granules throughout, or with rows of granules like chains, whilst the cyst may be split into two parts, an outer part of dark granules and a central gelatinous mass with various processes only slightly stained, or the whole area forms a network of fibrils with scattered dark granules. Occasionally the gelatinous ectocyst forms a double loop fused in the centre, each chamber thus being separated (Pl. II. fig. 13). In certain cases it may be that rupture of the interstitial tissues takes place, so that the ectoplasm of two adjacent cysts fuses. Besides the characteristic translucent investment the larger cysts have the same substance in their interior, and it gives rise to numerous striking figures—from solid central masses to brush-like or arborescent strands and intricate reticulations, the latter affecting in some instances a double chamber (Pl. IV. fig. 16). The size of the cysts ranges from ·5 mm. (Pl. I. fig. 12) to 8 or 9 mm. or more. Early stages of the cysts are also shown in Pl. II. (fig. 14) with undefined walls, and so close were they that their oval shape was probably due to pressure. A faint ectocyst appears in the upper figure. In another minute stage (Pl. I. fig. 5 *a*) the cyst was U-shaped, and no granular contents were in the section. Occasionally a cyst occurs in the section in which the central ovoid mass is separate from the gelatinoid layers, and apparently retains its shape by the nature of its substance, which consists of stained granules each surrounded by a protoplasmic investment (Pl. IV. fig. 22). Whether this was due to the effects of the preparation for section or otherwise is doubtful, but it resembled the conditions in its allies. Such appearances were unconnected with the origin of the young cysts. In the majority of the larger cysts the large stained granules form a belt externally, but they varied in size, were often devoid of a gelatinous investment, and in no case could they be identified with spores. Again, swarms of oval spores occur in Weissenberg's *Glugea* in the stroma surrounding the cysts as well as in the external region of the cyst. His vegetative and other "Kernes" likewise differ. The occurrence of the secondary capsule and general cellular condition also diverges. Thus there was an essential difference between them and *Glugea*; yet there was much in common. The subdermal gelatinoid fibrils in this form (*Lymphocystis*) are less developed than in the second form, but they have the same character. They do not, however, penetrate as large fibrils into the body of the tumour, the translucent finely granular stroma, already described, occupying the whole of the interstitial region. It is true a slight development of the coarse fibrils here and there takes place between two cysts, but it does not extend far inward. Moreover, the boundary of the narrow subdermal gelatinoid layer internally—all round—is better defined than in the form on the tail.

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* Rep. Lancast. Sea Fish. 1904, pp. 65 & 66, pl. iii. fig. 3.

† Which I owe to the kindness of Prof. Stanley Gardiner, of Cambridge University. They were made by his assistant in the Laboratory, Mr. Drury.

Whilst no separate and definite layer intervenes between the structureless gelatinoid investment and the stroma around, the central mass often presents an entire margin, the granular contents adhering evenly exteriorly. In certain cases a distinct thin line envelops the granular contents, a feature due to the transference of the gelatinoid substance from the central region to the surface, and independently of the more conspicuous structureless investment. The histology of the cysts has been minutely studied by Woodcock, and he ends by asserting that each is an organic unit. After much discussion and comparison with *Lymphosporidium* of the brook-trout epidemic in America, he concludes "that *Lymphocystis* appears to combine, to a certain extent, Gregarine and Microsporidian characters with remarkable results."

In the preparations the cells presented numerous stained granules, large and small, and occasionally a large central "nucleus" surrounded by a dark ring; but the latter appeared to be only a phase in the arrangement of the mobile contents, and was subject to infinite variety.

Prof. Johnstone's * two slides of the same form from the skin of a sole (external to the scales) presented few and comparatively small cysts, but each had the structureless ectocyst or gelatinous investment and the granular contents. Two additional slides, from the same source, of the ovarian region of the cod (Sept. 1925) showed, in the first, part of the ovary (stained blue) with an "angio-sarcoma" in the centre (coloured red). In the delicate stroma several bodies like the Myxosporidian cysts occurred, but these and some in the tumour itself could not be identified satisfactorily. The latter differed from the true cysts in filling the space entirely, and were devoid of the characteristic ectoplasm. In the other preparation were certain large circular ova near the margin of the central tumour and in the centre of the latter itself, but they differed from the cysts. There were also certain large rounded masses, one showing a pale ectoplasm, and the mass appeared to be dividing into two, but the investing tissue was too dense and the smaller masses outside agreed with ordinary ova. The isolation of these (which stained like the tumour) and their structure differed from the conditions in the true cysts.

The Second Tumour.

The rays of the tail-fin in a plaice, from St. Andrews, of medium size were the seat of a diffuse and somewhat nodulated tumour (Pl. II. fig. 21) which extended about half an inch from the right or lower edge to the dorsal or left edge, commencing in front behind the bony skeleton and passing backward to the extremities of the rays. The thick, firm, mass fixed the rays, and somewhat distorted the fin so that its functions were much interfered with. The rays of the distorted fin were almost indistinguishable on the left base either dorsally or ventrally, but on the right they were distinct from the base to the tip for an area fully half an inch in breadth, all beyond this area being involved in the tumour both dorsally and ventrally. The complete entanglement or absorption of the rays by the tumour was noteworthy, and consequently the fin was considerably shorter on the left side and generally asymmetrical. Little could be made out with the naked eye on section beyond a uniform solid tissue, which appeared to incorporate the the rays in its substance, surrounding them with a growth of firm tissue. Microscopically the external investment was akin to the normal, and to that covering the previous Myxosporidian tumour, viz., a superficial layer of cells or vacuoles, and a thicker inner layer of minute cells abutting on a deeply-stained belt of gelatanoid fibrils beneath.

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* I have to thank Prof. Johnstone for his kind courtesy on various occasions.

Within the foregoing is a series of cysts (Pl. IV. fig. 17), each showing a thick corrugated band that seems to be the homologue of the structureless ectoplasm of the previous form, and which frequently makes an incomplete investment, for it ends in a granular or reticulated mass at one side. In the larger cysts, however, the investment is often complete, the centre of the cyst being occupied by a translucent reticulated mass with small clear vesicles, thus differing from the condition in the previous Myxosporidian. The stained gelatinous investment (amœboid) often forms a mass at one end (Pl. IV. fig. 16). The cysts rarely extend into the dermal tissue, but lie in the subdermal fibro-gelatinoid layer, and each has its opaque band (stained), which occasionally is spirally rolled. In certain spaces, again, large masses of the gelatinoid substance occur near dense fibroid growths in the interstitial tissues, thus wholly differing from the condition in the previous form.

The subepidermal gelatinoid layer forms considerable offshoots here and there with the cysts in it; indeed, it seems to be the only tissue in which the cysts are, and it always has a coarse fibrillar aspect from the parallel threads or chain-like tissue. These fibres show constrictions and dilatations, especially on the inner border of the subepidermal layer (Pl. IV. fig. 18). The occurrence of these slender parallel fibrils of the gelatinoid substance throughout the entire tumour is characteristic, and they sometimes lie in the centre of 10 or 12 cysts, processes passing between them.

In the sections the subepidermal layer of fibrils occasionally throws out a leaf-like ridge having very fine ramifications of its fibres (Pl. IV. figs. 3 & 19), a central trunk at the base leading with others, which are lateral, into the ridge. The fibres inosculate with each other in their course. In some of the cysts, again, translucent reticulations (protoplasmic) radiate from a central mass.

The colour of the gelatinoid masses in the stained sections is by transmitted light slightly brown, like the belts in the cysts, whilst the other tissues are bluish, except the finely-reticulated interstitial tissue and the central reticulation of the cysts. In certain slides the outer edges of the interstitial tissue are also tinted bluish. The breaking-up of two large gelatinoid masses into finely-reticulated fringes, which may join the folded interstitial tissue, is a prominent feature, and the amalgamation is complete. The coarser gelatinoid tissue seems in this form to take the place of the finer translucent tissue forming the general stroma in the former species.

It stains slightly, but sometimes not at all in the central parts, and is thus in contrast with the subdermal and other parts of the gelatinoid fibrillar tissue.

When crushed from their position (centre) in a section on a slide, the cells of this form sometimes cling together, as in Pl. III. fig. 23, a feature not hitherto seen in the other type. Such would appear to indicate that the surrounding tissue forms a more definite boundary-wall than in the latter. The stained ectoplasm is seen in two of the cysts in the figure.

Viewed broadly, much of the area of this tumour in section is occupied by curiously folded translucent masses (Pl. II. fig. 24) with numerous small blood-vessels. The tissue, indeed, resembles the folding or doubling of endless tubes, and is probably a product of the prevalent gelatinoid tissue, which forms a border to it, and in which the blood-vessels lie. The tissue varies in appearance, being more loosely or more finely reticulated, and sometimes ending in thread-like processes at a corner. Some of the masses, again, near the opaque bands of gelatinoid substance are formed of closely-arranged fibres so that they are less transparent, the one often joining the other by a coarsely or a finely-branched border. With the exception of the blood-vessels, the entire tumour, within its investment, is constructed of the same gelatinoid tissue in its several modifications, with the addition of the Myxosporidian parasites. The presence of the latter is probably the cause of this remarkable growth, which, however, assumes, by its incorporation of the fine rays and its great vascularity, a more or less malignant aspect. It is further interesting that a somewhat finer variety of the same translucent gelatinoid tissue occurs in the interior of each Myxosporidian in the tumour. Thus a striking uniformity is maintained throughout the mass.

The walls of the large blood-vessels are formed of firm fibres, the blood-corpuscles occupying the centre, and smaller trunks are shown (Pl. II. fig. 24, *b.v.*). The tumour is throughout highly vascular, and evidently in a state of active function.

The differences between this and the former Myxosporidian rest in the greater development of the gelatinoid fibrillæ in the present form, and the substitution of the irregular strands of the same substance for the much finer fibro-granular stroma of the former tumour, as well as in the nature of the cysts with their translucent and finely-reticulated gelatinoid contents. Moreover, developing forms are there present, whereas in the tumour on the tail such are only represented by the slightly smaller processes at the margin—under the dermal layer. No minute forms or spores were seen. The facies of the two differed. The large cysts in the tumour from the tail were studded in single file along the surface with a broad belt of the fibro-gelatinoid layer internally with other cysts.

Glugea in section somewhat resembles the first-mentioned tumour; but there is no ring of spores, only the structureless ectocyst, nor is the swarm of oval spores present in the stroma between the cysts.

These tumours appear to belong to the group of Phænocystes or intercellular parasites, in contradistinction to the Cryptocystes or cellular parasites. The trophic stage seems to be amœboid, as shown in the varied shapes assumed in the sections, the gelatinous exterior often forming lobate processes, whilst the interior is granular. Nothing in the life-history, so far as known, is comparable to the complex cycle of such as the Coccidian, *Aggregata eberthi**, in which schizogony occurs in the gut of *Portunus depurator,* whilst the merozoites which penetrate the intestinal wall of the cuttlefish grow into large mero- and smaller microgametocytes.

The origin of these parasites is at present in obscurity, but it may be connected with a crustacean such as *Portunus* or an annelid like *Lagis koreni*, the latter carrying a gregariniform parasite which develops into *Eugregarinellospora lagidis.*

EXPLANATION OF THE PLATES.

Plate I.

Fig. 1. Dorsum of plaice with pedicled tumour; 1 *a*, ventral surface with four small tumours.

Fig. 2. Cyst with double layer of ectocyst.

Fig. 2 *a*. Tumour on head of plaice enlarged.

Figs. 4 & 4 *a*. Varieties in the shape of the smaller cysts in the first type.

Fig. 5. Blood-vessel containing foreign body. × 360.

Fig. 5 *a*. Minute cyst with U-shaped gelatinoid mass. × 200.

Fig. 6. Small cyst showing translucent ectocyst, and stained (opaque) centre.

Fig. 7. Section of the wall of the tumour. *a*, superficial cells; *b*, minute cells; *c*, gelatinoid fibrilla layer; *d*, cyst.

Fig. 7 *a*. Superficial epidermal vesicles on the surface of the tumour. × 350.

Fig. 12. Early cyst (opaque) without trace of ectocyst externally.

Fig. 20. Small cyst in which the ectocyst touches the surrounding stroma. × 60.

Plate II.

Fig. 13. A large cyst in which the gelatinoid ectocyst forms a double cavity (*a* & *b*) after preparation. × 60.

Fig. 14. Two minute developing cysts, each with traces of the ectocyst externally, the granular centre being stained. × 60.

Fig. 15. A group of small cysts of nearly uniform size. × 60.

Fig. 21. Tail of a plaice bearing a malignant (?) tumour incorporating many of its rays. Nearly natural size.

Fig. 24. Section of a portion in the centre of the foregoing tumour showing the gelatinoid fibres and blood-vessels at the margin, and the complete tube-like arrangement of the central tissue. × 60.

Plate III.

Fig. 8. View of a portion of a multiple tumour (*Lymphocystis*) with developing cysts of various sizes, and a larger one below. *ec.*, ectocyst; *g.*, granular centre; *v.*, blood-vessel. × 80.

Fig. 23. Three adherent cysts from the tumour in the tail. × 60.

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* Biol. Rev. Biol. Proc. Camb. Philos. Soc.p. 163, April 1924.

PLATE IV.

Fig. 3. Bifid ridge from the subcutaneous fibro-gelatinoid layer. × 60.

Fig. 16. Section of two cysts from the foregoing tumour, the left with the ectocyst ending in a mass, the right having the ectocyst all round. × 60.

Fig. 17. *Section of cysts from the surface of the tumour of the tail.* × 60.

Fig. 18. Fibre-like strands, with dilatations and contractions of the subcutaneous layer from the tumour of the tail. × 60.

Fig. 19. Section of a ridge of the same layer showing a leaf-like pattern. *a*, areolar surface-layer; *b*, finely cellular layer. × 60.

Fig. 22. Section of a cyst from the head of the first-mentioned plaice in which the contents appeared to be cellular, though probably a result of preparation.

VI.—*Notes on Neotropical* Pselaphidæ (*Coleoptera*), *with Descriptions of new Species.* By FRANK C. FLETCHER, Minneapolis, Minn., U.S.A.

THIS is the first of a series of short papers on South American Pselaphidæ, in which I shall give descriptions of miscellaneous new species, notes on others, and revisions of small groups of species.

Contributions to this fauna already published will be found in Ann. Ent. So. Amer. 1928, xxi. pp. 203–230; Trans. Amer. Ent. Soc. 1928, liv. pp. 69–77; and Ent. News, 1927, xxxviii. pp. 149–153.

Unless otherwise stated, all types are to be found in the personal collection of the author.

Arthmius (*Arthmius*) *scaphiger*, Sharp, Biol. Centr.-Amer. ii. 1, 1887, p. 13.

Described as coming from Mexico with query, not recorded since. There is a single male in my collection from Jalapa, Mexico.

Arthmius (*Arthmius*) *subfusus*, sp. n.

♂. Elongate, narrowed anteriorly; bright rufo-testaceous, abdomen darker; scarcely perceptibly punctulate, strongly shining; pubescence pale, sparse, and rather short.

Head quadrate, including eyes considerably wider than prothorax; eyes very large, convex, coarsely faceted; dorsal surface very smooth, evenly and slightly convex over the entire surface, no impressions or foveæ of any kind; front and epistoma evenly declivitous, continuous with the vertex; sides evenly rounded; antennal tubercles not prominent.

Antennæ slender; second segment oval; third somewhat transverse, broader at apex, produced on outer side; fourth very transverse, dilated, one-half wider than second, the inner surface somewhat concave, covered with glandular hairs; fifth of about the same form as fourth, but wider and somewhat produced on outer side, surface likewise covered with glandular hairs; sixth greatly expanded on outer side, auriculate, fully twice as broad as second, the edge fringed with dense white hair; seventh subquadrate, narrowed, not wider than second; 8 of about the same form, but slightly wider and more transverse, 9 and 10 subglobular; 9 distinctly wider than 8, 10 wider than 9, 11 elongate-conical, about equal to the three preceding together; the last three segments forming a distinct club.

Prothorax about equal in length and breadth, widest in front of middle, strongly rounded, then rapidly but evenly narrowed to base; surface smooth, glabrous, convex, not sculptured, with the usual basal transverse sulcus not prolonged at the sides.

Elytra slightly transverse, widest in apical third; humeri evident, but not pronounced; surface convex, with fine sutural striæ, but no discal striæ; punctuation consisting of minute scattered punctures, each bearing a hair.

Abdomen with last ventral large and broadly concave.

Legs modified as follows: anterior tibiæ swollen in middle and slightly notched at outer side near apex; posterior femora with a thin line of fine pale pubescence along the inner length; posterior trochanters with white hair.

Length 1·6 mm.; breadth 0·8 mm.

One male, from Jalapa, Mexico.

This species belongs in that section of *Arthmius* characterized by the modified antennæ, but it is widely different from any of the described species. The type of antennal modification is unique in the genus, and this with the unsculptured head makes this species very easy of recognition.

Arthmius (*Arthmius*) *extraneus*, sp. n.

♂. Elongate, convex, narrowed anteriorly; dark testaceous in colour; not perceptibly punctate, very shining; pubescence pale and very sparse.

Head somewhat longer than wide; width including the eyes equal to that of the prothorax; eyes moderate, coarsely faceted; vertex slightly convex, sides without margins or carinæ; a pair of very deep sharp foveæ between the eyes, closer to them than to one another; these foveæ do not give rise to a sulcus; front just behind the antennal tubercles with a pair of small shallow impressions separated only by a ridge; front evenly declivitous to epistoma; antennal tubercles distinct, but not prominent, smooth.

Antennæ slender; segments 2 to 8 all longer than broad; second oval, slightly longer than broad; third a little narrower and very slightly obconic, one-half longer than broad; 4 of same form, length, and width; 5 of same length, more obconic, distinctly wider than 4 or 6; 6 a little shorter than 4, decidedly longer than broad, of same form; 7 just perceptibly wider than 6, of same form, a little over one-half broader than it; 8 much shorter, but still distinctly longer than broad, of same form and width; 9 suboval, distinctly wider, almost one-half longer than broad; 10 about equal in length and width, much wider, widest at middle; 11 not much wider than 10, elongate-conical, equal to the two preceding together; last three forming a fairly distinct club.

Prothorax just equal in length and breadth, strongly rounded in anterior half, then rapidly narrowed to base; disk very convex, with no sculpture other than the usual transverse basal sulcus.

Elytra slightly transverse, widest in apical third; humeri distinct; disk convex, with the usual sutural striæ, three basal foveæ on each elytron, and lack of discal striæ; surface very sparsely covered with minute asperities, each bearing a hair.

Legs simple, except for the anterior, which are modified as follows: femur with an acutely margined, very deep, circular fovea in the middle of its superior surface; the exterior edge of this fovea is prolonged upwards in a point; joined to this prolongation is a long, high, finely crenulated ridge, extending from the fovea longitudinally to almost the apex of the femur; apex of tibia with a bunch of rather long, apparently glandular hairs. Middle tibia with a distinct mucro near apex; middle trochanter without trace of any but the usual pubescence.

Under surface. Metasternum with a deep longitudinal sulcus; apical ventral segment with a very deep irregular fovea in apical half.

Length 1·9 mm.; breadth ·8 mm.

Described from one male from Corumba, Matto Grosso, Brazil.

This species is very closely related to *cicatricosus* and *brevicollis*, both described by Raffray. I have not seen a specimen of *cicatricosus*, but I have one of *brevicollis* in rather poor condition from the type-locality, Minas Geraes. *Cicatricosus* was described from Central Paraguay. To elucidate the differences between the three species, I append the following table:—

Antennal tubercles smooth.

Head with a semicircular sulcus interrupted at middle. Antennal segments only slightly longer than broad. Fovea of anterior femur oblong, without longitudinal carina. Middle trochanter with slight brush of hair. Terminal ventral segment impressed almost over its entire surface, with a little tubercle at middle .... *cicatricosus*, Raff.

Head with a deeper semicircular sulcus, likewise interrupted at middle, but with a little tubercle. Segments of antennæ a little longer than broad. Fovea of anterior femur oblong, without carina. Middle trochanter normal. Terminal ventral segment with a very deep fovea at middle .... *brevicollis*, Raff.

Head without trace of sulcus, but with two very approximate foveæ in middle behind antennal tubercles. Fovea of anterior femur absolutely circular, with high crenulated crest running longitudinally. Middle trochanter simple. Terminal ventral with a broad irregular depression in apical half, occupying about one-half of segmental width; this impression is suddenly deeper at the apical margin .... *extraneus*, sp. n.

Arthmius (*Arthmius*) *rubriculus*, sp. n.

♂. Slender, narrowed anteriorly; rufo-testaceous, elytra paler; hardly perceptibly punctulate, very shining; pubescence scattered, pale.

Head subquadrate, width including eyes very slightly less than that of prothorax; sides parallel, not margined; eyes moderate, coarsely faceted; entire front and epistoma, from one antennal tubercle to the other, evenly depressed, the surface almost vertical; the surface of the front and epistoma is smooth and shining, but covered quite thickly with minute tubercles, when viewed under high power each tubercle is seen to bear a fine bristle; vertex slightly convex, with a pair of large foveæ between the eyes, no sulcus; surface smooth and shining; antennal tubercles slightly prominent, rendered so by the depression of the front and epistoma.

Antennæ rather stout; first segment simple; second oval, slightly broader than the next; 3 not much longer than broad, narrower at base; 4 of the same length, width, and form as 3; 5 a little longer, of the same form and just perceptibly thicker; 6 shorter than 5, of same width as 4 and 5; 7 more oval, of same form as 6, just perceptibly wider; 8 almost quadrate, distinctly shorter than 7; 9 oval, broader, and as long as 7; 10 of about the same length, broader, widest at middle; 11 oval, acuminate at apex, slightly longer than the two preceding together, the last three segments forming a distinct club.

Prothorax almost one-sixth broader than long, sides widest and strongly rounded in apical half, then rather gradually narrowed to base; disk convex, smooth, sculptureless except for the usual basal transverse sulcus.

Elytra slightly transverse, widest in apical third; surface convex, with the usual sutural stria and the three foveæ at base of each elytron; no distal stria; surface sparsely covered with small points each with a hair, particularly conspicuous on the interval between the sutural stria and the suture.

Legs simple, except for the anterior femora, which are modified as follows: femur with a rather deep oval fovea in apical third; exteriorly to it the femur is cut by a transverse groove or notch. Middle tibia with a short, blunt, inconspicuous mucro near apex.

Under surface modified as follows. Metasternum with a deep longitudinal groove, the edges of which are rounded. Terminal ventral segment with a deep almost circular cavity with rounded edge in apical three-fourths, and occupying about two-fifths of the segmental width. Intermediate trochanter with the usual pubescence.

Length 1·4 mm.; breadth ·6 mm.

Described from one male from Corumba, Matto Grosso, Brazil.

Rubriculus is closely related to *cruralis*, Raffray, likewise described from Matto Grosso. It may at once be known by the peculiar cavity of the front and epistoma, the lack of any cephalic groove, and the anterior femur lacking any trace of a ciliated carina.

Arthmius (*Arthmius*) *mancus*, sp. n.

♂. Elongate, slender, narrowed anteriorly; rufo-castaneous in colour; not perceptibly punctate, very shining; pubescence pale, scattered.

Head quadrate, width, including eyes, about equal to that of prothorax; eyes moderate in size, coarsely faceted; vertex moderately convex, with a pair of deep foveæ near the eyes; slightly anterior to these foveæ the front is posteriorly slightly elevated above the surface, rendering it sharply defined from the vertex, from one side of the head to the other; the entire front is almost flat and descends almost vertically, the flat surface extending completely across the head, obliterating the antennal tubercles; this flattened surface is shining and thickly covered with small tubercles; before the insertion of the antennæ, before it joins the epistoma, the front is transversely concave, but still covered with the minute tubercles; the epistoma itself is prominent, and, like the front, is covered with the tubercles.

Antennæ long and slender; first segment simple; second elongate-oval, broader than the immediately succeeding; 3 and 4 of about the same form, obconic, 3 perceptibly thicker than 4, both equal in length to 2; 5 and 6 equal in width, 5 distinctly longer than 4; 5 to 7 subcylindrical, 6 of same form as 5; 7 subequal in length to 6, just perceptibly wider; 8 just slightly longer than broad, narrower than 7; 9 distinctly broader, about equal to 7; 10 suboval, broader, widest near apex; 11 elongate-conical, a little longer than the two preceding together, the last three segments forming a distinct club.

Prothorax about equal in length and breadth; sides widest and broadly rounded slightly in front of middle, then rapidly narrowed to base; surface convex, smooth, polished, sculptureless except for the transverse basal groove.

Elytra slightly transverse, widest in apical third, convex, with the usual sutural stria and three basal foveæ on each elytron; surface smooth, sparsely covered with minute tubercles each bearing a hair, the tubercles more distinct in a single row on the interval between the suture and its stria.

Legs simple, not modified in any way; middle tibia with a mucro at apex.

Under surface modified as follows: metasternum with a deep oblong foveæ at middle; first ventral segment with a thin, posteriorly-directed ligula, the last with a deep, somewhat transverse depression occupying its entire length and most of its width; intermediate segments very short.

Length 1·4 mm.; breadth ·6 mm.

Described from one male from Corumba, Matto Grasso, Brazil.

By abdominal and cephalic structure this is a species obviously belonging in the group containing *cruralis*, *cicatricosus*, *brevicollis*, and the just-described *rubriculus*, a grouping which was made by Raffray because of the modified anterior femora of the males. It is, indeed, remarkable that *mancus* should be so close to these and have absolutely simple anterior femora. In addition, *mancus* may at once be recognized by the sharp separation between front and vertex, ligula of first ventral, much larger excavation of the last ventral, and other characters.

VII.—*The Classification of the British Carboniferous Brachiopod Subfamily* Productinæ. By Helen M. Muir-Wood, M.Sc., F.G.S.

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During the last fifteen years much has been written on the subject of *Productus*, and more detailed investigation of the many species belonging to this genus has led to its subdivision into at least twenty genera or subgenera by Thomas, Chao, Fredericks, Muir-Wood, and others. There are, however, at least three well-defined groups of species still included in the genus *Productus* (sensu stricto). Recent researches have shown that this genus should be even more precisely limited to a small group of species having a peculiar internal structure.

The genus *Productus* was described by James Sowerby (1814, 'Mineral Conchology,' i. p. 153) as "an equilateral unequal-valved bivalve with a reflexed, more or less cylindrical, margin; hinge transverse, linear; beak imperforate; one valve convex, the other flat or concave externally." He also adds:—"His [Martin's] Conch. *Anomites productus* is a good type of the Genus, therefore, as the name *Anomites* must be laid aside, I have adopted his specific name as the Generic one, the character it expresses being also peculiar." Sowerby (*op. cit.* p. 158) renamed *Anomites productus* of Martin *Productus martini*, and describes it in 1821 (Min. Conch. iv. p. 15). Since the species *Anomites productus* (=*Productus martini*) was considered by Sowerby to be typical of his genus, it is in strict accordance with the Rules of Zoological Nomenclature to regard it as the genotype of *Productus*.

Confusion arose as Sowerby figured more than one species as *Productus martini*, and only one of these specimens is identical with *Anomites productus*, Martin. Following de Koninck's and Davidson's lead the species *Productus martini* was regarded as either identical with or a variety of *Productus semireticulatus* (Martin), itself an ill-defined species. In consequence of this, Dall (1877, Bull. U.S. Nat. Mus. viii. p. 58) quoted *Productus martini* Sowerby = *Anomites semireticulatus* (Martin) + *A. productus*, Martin, as the genotype of *Productus*; while Hall (1893, 'Palæontology New York,' viii. p. 325) quoted *P. martini*, Sowerby = *Anomites productus*, Martin = *A. semireticulatus*, Martin = *Productus semireticulatus* as the genotype. Later (1894, Eleventh Annual Report State Geol. p. 297) Hall and Clarke reduced this quotation of the genotype simply to *Productus semireticulatus*.

Productus semireticulatus was, therefore, regarded as the type of the genus *Productus* until I. Thomas (1914, Mem. Geol. Surv. Gt. Brit. Palæont. i. pt. 4, p. 258) quoted *P. productus* as the genotype. This was adopted by Chao in 1927 (Pal. Sinica, B. v. fasc. 2, p. 26) and by me in 1928 (Mem. Geol. Surv. Gt. Brit. Palæontology, iii. pt. 1, p. 35), when the species *P. productus* and *P. semireticulatus* were finally disentangled.

Investigation of the species *P. productus* (= *P. martini*, pars) has shown that it differs in internal structure from *P. semireticulatus* in having an extra shelly plate or diaphragm, which is developed round the anterior end of the visceral disk of the brachial valve and extends between the trails of the two valves, usually at right angles to them.

A similar shelly plate was found by Dr. Girty in the North American species, *P. elegans*, Norwood & Pratten, and this species became the type of his genus *Diaphragmus*. Since the two genera *Productus* and *Diaphragmus* are characterised by a similar internal structure, *Diaphragmus* must be regarded as a synonym of *Productus*.

Productus thus becomes limited to a small group of species, including *P. productus* (Martin), *P. concinnus*, J. Sow., *P. carbonarius*, de Koninck, *P. redesdalensis*, Muir-Wood, *P. garwoodi*, Muir-Wood, etc. A new name is required for *Productus semireticulatus* and allied species, and also for such forms as *P. longispinus* and *P. lobatus*, all of which are at present grouped under the generic name *Productus*. The name *Dictyoclostus*, gen. nov., is therefore proposed for the *semireticulatus* group with *P. semireticulatus* as genotype, and *Eomarginifera*, gen. nov., is proposed for the *longispinus* group with *P. longispinus* as genotype.

Subfamily *Productinæ*, Waagen.

Productus, J. Sowerby, 1814 ('Mineral Conchology,' vol. i. p. 153), *emend.* H. M. Muir-Wood.

Genotype. *Anomites productus*, W. Martin (=*P. martini*, J. Sowerby, pars).

Syn. *Diaphragmus*, Girty (1910, Ann. N.Y. Acad. Sci. xx. pt. 2, no. 3, pp. 217, 218).

Diagnosis.—Shell elongate, both valves geniculate; hinge narrow; pedicle valve with long spreading trail. Flanks steep and posteriorly flattened. Shell costate in all growth-stages, costæ numerous, flexuous. Ribs few, seldom prominent. Spines set in rows on ears and cardinal slopes and scattered on trail. Teeth, dental sockets, and delthyrium absent. Marginal ridges narrow, short. A thin shelly plate or diaphragm developed round anterior margin of visceral disk of brachial valve, extending across space between trails of the two valves.

Species.—*Productus carbonarius*, de Kon., *P. concinnus*, J. Sow., ? *P. furcatus*, Muir-Wood *, *P. garwoodi*, Muir-Wood *, *P. elegans*, Norwood & Pratten, *P. productus* (W. Martin), *P. productus*, var. *hispidus*, Muir-Wood, *P. redesdalensis*, Muir-Wood.

Range.—*Syringothyris* zone to Upper Carboniferous.

Remarks.—This genus has not been found below the C. zone and the geologically earliest described species is *P. garwoodi*, which occurs in the C_1–S_2–D_1 sub-zones of Westmorland. This species, which was apparently developed from *P. rotundus*, Garwood, was probably the ancestor of *P. redesdalensis*, which occurs in the D_1–D_2 sub-zones of N. England and of Scotland. *P. redesdalensis* probably gave rise to *P. carbonarius*, which ranges from D_2 sub-zone up to the Upper Carboniferous. The interior of *P. furcatus* is at present unknown, and this species is doubtfully referred to the genus *Productus*. *P. concinnus* and *P. productus* were probably derived from a form resembling *P. furcatus*.

The distinguishing character of *Productus* is the diaphragm which extends across the narrow space between the trails of the two valves and closes the entrance to the visceral cavity. The diaphragm must therefore have been either porous or movable, in order to admit the passage of water into the shell.

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* Ref. Muir-Wood, Mem. Geol. Surv. Gt. Brit. Palæont. i. pt. 4 (1928).

DICTYOCLOSTUS, gen. nov.

Genotype. *Anomites semireticulatus*, W. Martin (in part.), Petrificata Derbiensia, p. 7, pl. xxxii. figs. 1, 2, pl. xxxiii. fig. 4 (Wigan, 1809).
Syn. *Productus*, J. Sowerby (in part.).

Diagnosis.—Shell elongate or quadrate in outline. Hinge moderately wide; pedicle valve evenly convex or produced into a short curved trail, brachial valve concave or geniculate. Costate in all growth-stages, costæ often prominent, bearing numerous spine-bases. Spines also in rows on ears and cardinal slopes. Ribs on visceral disk numerous and forming net-like ornament by enlargement at point of intersection with costæ. Diaphragm absent. Marginal ridges prominent, extending along hinge. Hinge-teeth, sockets, and cardinal area not developed.

Species.—*Productus antiquatus*, J. Sow., *P. bristolensis*, Muir-Wood, *P. costatus*, J. de C. Sow., ? *P. flexistrius*, M'Coy, *P. griffithianus*, de Kon., *P. hindi*, Muir-Wood, and var. *wettonensis*, Muir-Wood, *P. howratensis*, Muir-Wood, *P. insculptus*, Muir-Wood, *P. kilbridensis*, Muir-Wood, *P. multispiniferus*, Muir-Wood, *P. muricatus*, Phill., *P. pinguis*, Muir-Wood, *P. projectus*, Muir-Wood, *P. pugilis*, Phill., and mut. *senilis*, Muir-Wood, *P. rotundus*, Garwood, *P. scoticus*, J. Sow., *P. semireticulatus* (Mart.), *P. sulcatus*, J. Sow., *P. teres*, Muir-Wood, *P. vaughani*, Muir-Wood.

Range.—*Zaphrentis*-zone to Permian.

Remarks.—This genus ranges throughout the British Lower Carboniferous and also occurs abundantly in the marine Upper Carboniferous of Europe and North America, as well as in the Permian.

Dictyoclostus is distinguished from *Productus* by the absence of a diaphragm, by its wider hinge, less spreading trail, more prominent and less flexuous costæ.

EOMARGINIFERA, gen. nov.

Genotype. *Productus longispinus*, J. Sowerby, Mineral Conchology, vol. i. 1814, p. 154, pl. lxviii. fig. 1.
Syn. *Productus*, J. Sowerby (in part.).

Diagnosis.—Shell small, quadrate or elongate in outline. Pedicle valve evenly convex or slightly geniculate, with cincture often separating visceral disk from trail, brachial valve concave or geniculate. Costate in all growth-stages, costæ usually fine. Ribs slightly enlarged at point of intersection with costæ. Spines few, not increasing in number in senile stage, six spines symmetrically developed. Exterior of brachial valve with lamellose thickening round anterior and lateral margins. Interior of brachial valve with thickened shelly ridge, bearing slight crenulations, extending from cardinal process round lateral margins.

Species.—*Productus derbiensis*, Muir-Wood, *P. lobatus*, J. Sow., and var. *flexus*, var. *laqueatus*, Muir-Wood, *P. longispinus*, J. Sow., *P. minutus*, Muir-Wood, *P. præcursor*, Muir-Wood, *P. pseudoplicatilis*, Muir-Wood, *P. setosus*, Phill., *P. tissingtonensis*, Sibly, *P. triquetrus*, Muir-Wood.

Range. — Lower Carboniferous, ? C zone to Upper Carboniferous.

Remarks.—This genus is distinguished from *Productus* by the absence of a diaphragm. The symmetrical arrangement of six spines—one on each cardinal extremity, two on the front of the shell below the visceral disk, and one on the posterior part of each flank—distinguishes it from both *Productus* and *Dictyoclostus*. *Eomarginifera* is distinguished from *Marginifera* by the less-marked marginal ridges in the brachial valve and the absence of these ridges in the pedicle valve, also by the lack of crenulations on the exterior of the marginal ridges of *Eomarginifera*. The ornament and arrangement of the spines of *Eomarginifera* are also distinct from those of *Marginifera*. The latter genus is confined to the Upper Carboniferous and Permian.

CLASSIFICATION OF THE *PRODUCTINÆ*.

A considerable amount of overlapping is shown in the researches of Chao, Fredericks, Sarytcheva, and Whitehouse on the subject of the classification of the Productinæ and the following pairs of genera are synonymous. It is unfortunate that Fredericks' genera are described in Russian, with only a short *résumé* in English, and that many of his genera are vaguely described:—

Sowerbina, Fredericks, 1928 (Bull. Com. Géol. Leningrad, xlvi. 7, p. 789): genotype, *P. timanicus*, Stuckenberg = *Horridonia*, Chao, 1927 (Pal. Sinica, B. v. fasc. 2, pt. 1, p. 24): genotype, *P. horridus*, J. de C. Sow. (includes also *P. timanicus*).

Ruthenia, Fredericks, 1928 (*loc. cit.* p. 789): genotype, *P. irginæ*, Stuckenberg (includes also *P. humboldti*, d'Orb., and *P. purdoni*, Dav., etc.) = *Waagenoconcha*, Chao, 1927 (*loc. cit.* p. 85): genotype, *P. humboldti*, d'Orb. (includes also *P. irginæ* and *P. purdoni*).

Cora, Fredericks, 1928 (*loc. cit.* p. 790): genotype, *P. cora*, d'Orbigny [also *Euproductus*, Whitehouse, 1928, nom. nud. (Rept. Aust. Ass. Adv. Sci. xviii. p. 281)]: genotype, *P. cora*, d'Orb. = *Linoproductus*, Chao, 1927 (*loc. cit.* p. 128): genotype, *P. cora*, d'Orb.

Cancrinella, Fredericks, 1928 (*loc. cit.* p. 791): genotype, *P. cancrini*, De Vern., ? = *Linoproductus*, Chao, 1927.

Gigantella, Sarytcheva, 1928 (Mem. Geol. Sci. Res. Inst. Moscow, Geology, p. 13): genotype, *P. giganteus* (Martin) (includes also *P. edelburgensis*, Phill., and *P. latissimus*, J. Sow.) = *Kansuella*, Chao, 1928, pars (Pal. Sinica, B. v. fasc. 3, pt. 2, p. 67): genotype, *K. kansuensis*, Chao (includes also *P. giganteus* and *P. edelburgensis*).

Key to the Classification of the British Productinæ.

A. SHELL COSTATE IN ALL GROWTH-STAGES.

1. Shell ornamented by ribs and costæ on the visceral disk and anteriorly by costæ only. Costæ bifurcating, intercalations rare.
   - (*a*) With diaphragm .... *Productus*, J. Sowerby, 1814, emend. Muir-Wood, 1929 (see p. 102).
   - (*b*) Without diaphragm .... *Dictyoclostus*, Muir-Wood, 1929 (see p. 103).
   - (*c*) Marginal ridge in interior of brachial valve. Shell small, with six spines symmetrically arranged on pedicle valve .... *Eomarginifera*, Muir-Wood, 1929 (see p. 103).
2. Shell costate and ribbed on visceral disk, costate on trail, both valves geniculate. Cardinal area in pedicle valve with delthyrium closed by deltidium ...... *Sinuatella*, Muir-Wood, 1928.
   Genotype: *P. sinuatus*, de Kon.
3. Shell convex (not geniculate), ornamented by costæ and well-marked concentric growth-lines .... *Thomasia*, Fredericks, 1928.
   Genotype: *P. margaritaceus*, Phill.
4. Shell ornamented by fine costæ and numerous intercalations, usually with broad wrinkles on lateral slopes.
   - (*a*) Shell regular, quadrate, pedicle valve highly convex or geniculate .... *Linoproductus*, Chao, 1927.
     Genotype: *P. cora*, d'Orbigny; also *P. corrugatus*, M'Coy, *P. hemisphericus*, J. Sow., *P. koninckianus*, de Vern., *P. undatus*, Defrance.
   - (*b*) Shell irregular or elongate-triangular, tapering to umbo, pedicle valve slightly convex .... *Striatifera*, Chao, 1927.
     Genotype: *P. striatus* (Fischer de Waldheim).
   - (*c*) Pedicle valve cylindrical, brachial valve operculiform .... *Proboscidella*, Oehlert, 1887.
     Genotype: *P. proboscideus* de Vern.; also *P. ermineus*, de Kon.

5. Shell large, massive, hinge long. Costæ fine, irregular. Ribs developed posteriorly.
   (*a*) Cardinal area rarely developed on pedicle valve. .... *Gigantella*, Sarytcheva, [1928.
   Genotype: *P. giganteus* (Martin); also *P. latissimus*, J. Sow., *P. maximus*, M'Coy, *P. edelburgensis*, Phill.
   (*b*) Cardinal area developed in both valves, delthyrium closed by deltidium in pedicle valve .... *Kansuella*, Chao, 1928, emend. H. Muir-Wood, 1929.
   Genotype: *K. kansuensis*, Chao. Probably includes certain undescribed British species.

B. SHELL SPINOSE IN ALL GROWTH-STAGES.

6. Shell ornamented by numerous scattered spine-bases which are anteriorly elongated. Ribs faintly developed on cardinal slopes .... *Krotovia*, Fredericks, [1928.
   Genotype: *P. spinulosus* (Martin); also *P. aculeatus* (Martin).
7. Shell ornamented by elongated spine-bases and concentric ribs.................... *Pustula*, I. Thomas, [1914.
   Genotype: *Productus pustulosus*, Phill.; also *Pustula distorta*, Thomas, *P. interrupta*, Thomas, *P. magnituberculata*, Thomas, *P. nodosa*, Thomas, *Pr. ovalis*, Phill., *P. pilosa*, Thomas, *Pr. pyxidiformis*, de Kon., *Pr. rugatus*, Phill., *P. subpustulosa*, Thomas, *P. tenuipustulosa*, Thomas.
8. Shell ornamented by broad concentric bands bearing rows of spine-bases .... *Echinoconchus*, Weller, [1914.
   Genotype: *Productus punctatus* (Martin); also *P. elegans*, M'Coy, *Pustula subelegans*, Thomas, *P. venusta*, Thomas, *P. defensa*, Thomas, *P. exquisita*, Thomas, *P. eximia*, Thomas.
9. Shell ornamented by concentric bands bearing one row of spine-bases. Brachial impressions spoon-shaped .... *Overtonia*, Thomas, [1914.
   Genotype: *P. fimbriatus*, J. de C. Sow.

C. SHELL SPINOSE AND COSTATE.

10. Shell ornamented by spines posteriorly and costæ anteriorly .... *Avonia*, Thomas, emend. [Muir-Wood, 1928.
    Genotype: *P. youngianus*, Dav.; also *P. bassus*, Vaughan, *P. davidsoni*, Jaross, *P. keyserlingianus*, de Kon.

D. SHELL COSTATE, RIBBED, AND SPINOSE.

11. Shell ornamented posteriorly by ribs and by costæ bearing elongated spine-bases, and anteriorly by flattened bands bearing

rows of spine-bases. Median septum posteriorly bifurcating .... *Buxtonia*, Thomas, 1914, emend. Muir-Wood, 1928.
Genotype: *P. scabriculus* (Martin), also *P. scabriculo-costatus*, Vaughan.

E. Shell ribbed.

12. Shell ornamented by prominent concentric ribs. Anterior margin surrounded by ribbed rim projecting at right angles to shell .... *Thomasella*, Fredericks, [1928.
    Genotype: *P. wrighti*, Dav.
13. Shell ornamented by concentric ribs, and attached by cementation or by spines along hinge of pedicle valve .... *Etheridgina*, Oehlert, [1887.
    Genotype: *P. complectens*, Etheridge.
14. Shell ornamented by ribs and large scattered spines .... *Plicatifera*, Chao, 1927.
    Genotype: *P. plicatilis*, J. de C. Sow.; also *P mesolobus*, Phill., ? *P. carringtonianus*, Dav.

F. Shell smooth.

15. Shell ornamented by large spines and growth-lines, and rarely by faint traces of costation .... *Horridonia*, Chao, 1927.
    Genotype: *P. horridus*, J. de C. Sow.

The precise range of many of these genera is uncertain. *Horridonia* is apparently limited to the Permian. *Thomasia* and *Thomasella* occur in the Upper *Dibunophyllum*-zone, but may range upwards. *Kansuella* is possibly confined to the Lower Carboniferous, and occurs in the *Dibunophyllum*-zone. *Gigantella* and *Striatifera* are not known below the *Seminula*-zone, and are especially characteristic of the Upper *Dibunophyllum*-zone, but they extend up into the Upper Carboniferous or even into the Permian. *Productus*, *Linoproductus*, *Plicatifera*, and *Eomarginifera* were probably evolved in Upper *Zaphrentis* or Lower *Syringothyris* times, but became more abundant in D_2. *Linoproductus* and *Productus* extend up to the Upper Carboniferous. *Buxtonia*, *Pustula*, *Echinoconchus*, *Avonia*, and *Dictyoclostus* appear in the *Cleistopora*-zone or early *Zaphrentis* times, and range throughout the Carboniferous.

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(For more complete lists, see Muir-Wood and Thomas.)

VIII.—*Descriptions and Records of Bees.*—CXXI.

By T. D. A. Cockerell, University of Colorado.

Andrena kuznetzovi, sp. n.

♀ (type).—Length 13·7 to 14·7 mm.

Head, thorax, and legs black; abdomen shining green, the depressed parts of the tergites bluish green, the first tergite purplish black except apically, the second suffused with purplish black across the middle, the third to fifth with the elevated part yellowish green; hair of head and thorax long and thin, rather dull white, black at apex of clypeus, on vertex, across middle of thorax, between wings (but thin), and on legs, but anterior femora with long white hair behind, middle femora with some white hair above, hind femora with a white fringe in front, and the large curled floccus pure white; abdomen without bands, caudal fimbria greyish black, with long white hairs overlapping and at sides; facial quadrangle broader than long, very long white hair at sides of face; malar space linear, but evident; mandibles ordinary; process of labrum very broad, rounded; clypeus finely and densely rugoso-punctate, but glistening, with a delicate median raised line; front striate; flagellum dusky reddish beneath, except at base; third antennal joint long, exceeding next two together; facial foveæ dark chocolate-brown, moderately broad, running close to orbits, and ending much below level of antennæ; mesothorax dull and minutely granular, except the posterior middle, which is shining and sparsely punctured; scutellum bigibbous, the elevations shining, the surface much more closely punctured than posterior part of mesothorax, but on each side a little space with few punctures; area of metathorax triangular, poorly defined, minutely rugulose, with feeble irregular plications (hardly evident under lens) at base; mesopleura dullish; tegulæ black. Wings long, hyaline, the upper portion and apex suffused with pale brown; basal nervure meeting nervulus; second cubital cell very broad, receiving recurrent nervure slightly or considerably beyond middle; third cubital shorter than usual; spurs black; second tergite depressed in middle about a third. Surface of abdomen under microscope minutely tessellate, with sparse, very minute, piliferous punctures; under a lens the abdomen appears impunctate.

♂.—Length about 12 mm.

With the usual sexual differences; face very broad; mandibles long but stout, with an inner tooth; face with long pure white hair, but much black at sides; flagellum long, dark brown beneath; third antennal joint not as long as next two together, the fifth being unusually long; thorax with long white hair, black on disc of scutellum; stigma narrow, red with a dark margin; abdomen shining steel-blue.

Tashkent, Usbekistan, March 25, 1926; many females and two males (*N. Kuznetzov*).

A fine species of the group of *A. cineraria*, L., in the Central Asian fauna to be compared with *A. metallescens*, Ckll., from Tamerlan-Kuporjuk, which has the caudal fimbria fulvous, and with *A. peregrina* (Smith), from Yangihissar, which has the wings with a deep fuliginous cloud and the female abdomen dark purple.

There is some general resemblance to *A. ferghanica*, Mor., which is rather large, with the hair on the thorax grey. The male has the abdomen much more polished than in *A. cineraria* (L.).

Andrena kuznetzovi, form *micrander*, nov.

On the same day and also on March 21 Prof. Kuznetzov took numerous males, 9 to 9·5 mm. long. I set these aside as a different species, but they have no valid characters, and I find the genitalia of the large and small males to be exactly alike. It is thus evident that the male of this species is sharply dimorphic as to size.

Andrena brevipalpis, sp. n.

♀.—Length about or hardly 10 mm., anterior wing 7.

Black, rather slender; head and thorax with erect hair, fulvous dorsally, pale greyish on face, cheeks, and pleura; facial quadrangle about square; malar space linear; mandibles ordinary; process of labrum broadly truncate; clypeus thinly hairy, shining, but with a minutely tessellate surface, with widely scattered large punctures, the middle line impunctate but not elevated or polished; front striate; third antennal joint slightly longer than next two together; flagellum ferruginous beneath except at base; facial foveæ moderately broad, pale clear ochreous, close to orbits, extending below level of antennæ; mesothorax dullish, but shining on disc, the surface minutely tessellated and rather sparsely (hardly noticeably under lens) punctured; scutellum shining; area of metathorax poorly defined, entirely dull and rugulose, without plicæ; lower part of mesopleura somewhat shining; tegulæ rufo-fulvous. Wings hyaline, slightly dusky; stigma not very large, pale fulvous with dark margin, nervures pale fuscous; basal nervure falling short of nervulus; second cubital cell rather small, a little higher than long, receiving recurrent nervure at about the end of the third fifth. Legs black, with pale hair, light rufo-fulvous on inner side of tarsi; tibial scopa ample and rather loose, very pale fulvous, the hairs on outer side simple; claws bifid; scopa of hind femora very long and white. Abdomen moderately shining, dull in some lights, so finely punctured as to appear practically impunctate under a lens; second tergite in middle depressed less than half but more than a third; tergites 2 to 4 with narrow, dense, very pale ochreous hair-bands, broadly interrupted on second; caudal fimbria dark brown.

Boulder, Colorado; one ♀ captured on the window of my office at the University of Colorado, June 26, 1929.

It has almost exactly the aspect of *Iomelissa violæ*, Rob., and looked at from behind could be supposed identical; but the face is much narrower and the palpi are short, whereas in *Iomelissa* they are much elongated. In Viereck's Connecticut table it runs to *A. novæangliæ*, Vier., but it is not that.

Andrena basifusca, sp. n.

♀.—Length about 12 mm.

Robust; head, thorax, and legs black, abdomen dark purple-blue; first tergite mainly black, with apical margin blue; second shining black, with the depressed part brilliant purple; third and fourth purple, blue along the margins of the depression; fifth blue, with apical fimbria black; sides of face with long white hair, vertex and cheeks with black hair; thorax anteriorly and posteriorly with white hair, but black between the wings; sides of thorax with black hair, but white on tubercles, and upper part of mesopleura with some long white hairs. Abdomen bare. Legs with black hair, long white hairs on anterior femora behind, and basal floccus of hind legs white; facial quadrangle broader than long; malar space linear; clypeus glistening but not polished, closely punctured, with a strong median ridge; flagellum very obscurely brownish beneath; third antennal joint longer than the next two together; foveæ not very broad, dark brown, separated from eye by a wide shining band; mesothorax and scutellum densely punctured but glistening; mesothorax polished posteriorly, but scutellum hardly so anywhere; area of metathorax triangular, rugulose, with feeble plicæ at base; tegulæ black, a little reddish posteriorly. Anterior wings deep fuliginous, violaceous, the brown colour extending to base; basal nervure meeting nervulus; second cubital cell very broad, receiving recurrent nervure beyond middle; stigma small and black; second tergite in middle depressed more than a third but less than half. Abdomen shining, without evident punctures.

Ak-Tasch Mountains, Usbekistan, June 19, 1926 (*N. Kuznetzov*).

Very like *A. peregrina* (Smith), but easily distinguished by the wings not being hyaline at base.

Also resembles *A. hemicyanea*, Ckll., but the wings not longitudinally bicoloured, and clypeus different. It may also be compared with *A. fumipennis*, Schm., but that has a quite different clypeus and wings not so dark.

Andrena zachroa, sp. n.

♀.—Length about 11·2 mm.

Head and thorax black, with stiff very rich ferruginous-red hair, dense on sides of face and about antennæ, on sides of mesothorax and scutellum, and on postscutellum, but very sparse on clypeus and discs of mesothorax and scutellum; malar space linear; mandibles very faintly reddened about middle; labrum black, the process truncate; antennæ black, third joint nearly as long as next two combined; clypeus flattened, dull, minutely and densely punctured, with a delicate median raised line; facial foveæ broad, but very inconspicuous, largely overlapped by the spreading red hair; cheeks shining; mesothorax dull, slightly shining, very finely and closely punctured, microscopically tessellate between the punctures; posteriorly the mesothorax is more shining, and the scutellum is shining; area of metathorax entirely dull and granular, without plicæ, and defined only by absence of hair; mesopleura dull; tegulæ shining dark red. Wings strongly reddened; stigma moderate, dull ferruginous, with darker margin; nervures fuscous; basal nervure going basad of nervulus; second cubital cell about square, receiving recurrent nervure a little beyond middle; third cubital long. Legs black, with anterior tibiæ apically, and their tarsi, middle femora apically, and their tibiæ and tarsi, and hind femora, tibiæ, and tarsi all red; scopa of hind legs bright red; spurs red; middle basitarsi broad. Abdomen flattish, mostly bare, moderately shining, reddish black, with the first tergite, sides of second, and transverse suffusion on third and fourth rather dark red; a large black spot at each extreme side of second; apices of segments 2 to 4 with broad, dense, very bright orange-fulvous hair-bands, very widely interrupted on 2, narrowly on 3, entire on 4; apical tuft red; venter black, with red hair-bands.

Tunis; no other data available.

One of the most beautiful species of the genus. It resembles *A. cirtana*, Lucas, which I saw in Mr. Morice's collection, and noted; very handsome shining red abdomen, first tergite black with red hind margin; hair of head and thorax entirely bright red. There is also a strong resemblance to *A. russula*, Lep., judging from the description, but that has the abdomen black, with the band on the fourth tergite interrupted. The length is given as 4½ lines, which appears too small; but *A. oraniensis*, Lep., is said to be 4 lines, and it is actually over 12 mm. long. It is possible that the present insect is a rufescent variety of *A. russula.*

Andrena melandura, Cockerell, 1922.

Andrena æmula, Alfken, 1926, is a synonym.

Andrena hemicyanea, sp. n.

♀.—Length about 13 mm., anterior wing 10·5.

Robust; head, thorax, and legs black; abdomen dorsally deep blue, shining, but the venter brownish black; head broad, facial quadrangle nearly square; mandibles black, malar space linear; sides of face with long, outstanding, very conspicuous white hair; occiput and upper part of cheeks with long white hair; lower part of cheeks, sides of vertex, and clypeus with black hair, on clypeus thin and not conspicuous; clypeus very densely and strongly punctured, glistening between the punctures, and with a strong shining median keel; process of labrum shining, broadly rounded, with sloping sides; facial foveæ dark chocolate-brown, moderately broad, going below level of antennæ, with only a linear separation from orbits; antennæ black, third joint very long, about equal to next two combined; thorax practically hairless above, tubercles conspicuously tufted with white hair; sides of metathorax with much white hair, forming a scopa; pleura very coarsely rugoso-punctate, with thin black hair; mesothorax shining, with scattered distinct punctures; scutellum similarly sculptured, the punctures very sparse on disc; postscutellum coarsely punctured, not hairy; area of metathorax large, dull, with coarse wrinkles, and defined by a rounded line (not at all squared off behind); tegulæ black. Anterior wings with the upper half deep fuliginous, violaceous, the lower portion and a space just beyond third discoidal cell hyaline; stigma narrow, reddish, with dark margin; nervures dark fuscous; basal nervure going well basad of nervulus; second cubital cell broad, receiving recurrent nervure a little beyond middle; third cubital about as broad on marginal as second. Legs with mainly black hair, but much white on anterior femora behind, on hind femora beneath, and scopa of hind tibiæ outwardly white; hair on inner side of hind basitarsi purplish black; spurs black. Abdomen broad, shining, practically hairless above, but with a dense black caudal tuft, the sides of fifth tergite with much white hair and of fourth with white tufts; surface of tergites polished, feebly punctured; second tergite in middle depressed less, but not much less, than one-half.

Tunis; no other data available.

Closely related to *A. agilissima* (Scopoli), for which it might be taken, but a little smaller, the raised part of second tergite less closely and evenly punctured; area of metathorax shorter and broader, more semicircular; mesothorax more shining and less closely punctured; third cubital cell more produced apically. *A. asperrima*, Pérez, departs from the *A. agilissima* type in the opposite direction.

Andrena kengracensis, sp. n.

♀.—Length 11·2 mm.

I had referred this to *A. flavipes* (Panzer), which is recorded from this region, and no doubt it has been so regarded. In the Tashkent Museum I saw a specimen from Tashkent labelled "*A. fulvicrus*, Kirby (=*flavipes*)," but whether it was *A. kengracensis* I cannot now say. On comparison with *A. flavipes* from Gray, France (*André*), the new species differs by the dull white hair of under surface of thorax and sides of face, which should refer it to *A. gravida*, Imh.; but it differs from *gravida* (from Hastings, *Sladen*) by the shorter hind basitarsi, with the hair on the inner side dark chocolate instead of lively pale reddish. The third antennal joint is much longer than the next two together, the fourth being short and transverse. In *A. gravida* the fourth joint is longer. The three abdominal bands of *A. kengracensis* are pure white, instead of having a pale ochreous tint as in *A. flavipes.* Thus, while the insect runs to *A. gravida* in the tables, it is, on the whole, a closer relative of *A. flavipes,* perhaps best regarded as a subspecies. The type-locality is Kengrak hills, 26–28 kilometres north of Tashkent, Usbekistan, in a stony desert, May 16, 1926, 4 ♀ (*N. Kuznetzov*). Also one from Ak-Tasch mountains, about 1250–1600 metres above sea-level, June 22, 1926 (*Kuznetzov*).

Andrena (*Ptilandrena*) *pronitens*, sp. n.

♀.—Length about 8 mm.

Black, with the small joints of the tarsi reddish; hair of head and thorax erect and abundant, pale ferruginous dorsally, long and bright on scutellum; hair of face (very thin), cheeks, and underside of thorax dull whitish; malar space very short; mandibles ordinary, very faintly rufescent subapically; process of labrum elevated, broadly truncate; clypeus strongly convex, highly polished and impunctate on disc, dull at extreme sides; front striate; facial quadrangle broader than long; antennæ black, third joint not very long, but as long as next two together, or nearly so; facial foveæ rather broad, pale brown, very conspicuous, ending below at level of antennæ, with only a linear separation from orbits; mesothorax dull, scutellum shining, mesopleura dull; area of metathorax large, triangular, dull, with very short plicæ (between which the surface is somewhat shining) at extreme base; tegulæ dark brown. Wings reddish hyaline, apically greyish; stigma large, clear ferruginous, approaching orange; nervures pale ferruginous; basal nervure falling short of nervulus; second cubital cell narrow, receiving recurrent nervure at beginning of its last third. Legs with pale fulvous hair, the tibial scopa very pale, not dense, on outer side with strongly plumose (pectinate) hairs, the branches not numerous. Abdomen rather broad, dullish, appearing impunctate, the microscope showing a minutely tessellate surface with excessively minute scattered punctures; second tergite in middle depressed less than a third; tergites 2 to 4 with narrow greyish-white hair-bands, very thin in middle of second; apex with very pale grey hair.

Geneva Park, Boulder, Colorado, May 14, 1929 (*Hugo Rodeck*).

Resembles *A. beckeri*, Ckll., but easily distinguished by the clypeus. There is, perhaps, little real affinity, as in *A. beckeri* the hairs on outer side of hind tibiæ are simple.

Another species with shining clypeus, taken at Boulder, is *A. flavoclypeata*, Smith. Robertson places this in his genus *Opandrena*, but actually the hair on outer side of hind tibia in the female is plumose.

Mr. Rodeck also took at Boulder *A. nasoni hartfordensis* (Ckll.), new to Colorado.

At Rifle, Colorado, Mr. S. A. Rohwer took *A. sapellonis*, Ckll., also new to Colorado.

Andrena azalearum, sp. n.

♀.—Length about 12 mm.

Not unusually robust; black, including mandibles, antennæ, tegulæ, and legs; hair of head and thorax white, but black on vertex, sides of face above, posterior part of mesothorax, and scutellum; legs with mainly white hair, pale ferruginous on inner side of tarsi, scopa of hind tibiæ bicoloured, white in front, black behind; abdomen dorsally bare, a little pale hair at sides, caudal fimbria black, ventral segments fringed with long glistening white hairs; facial quadrangle broader than long; malar space linear but evident; mandibles ordinary; clypeus convex, shining, distinctly and rather closely punctured, with no median ridge; process of labrum narrowly truncate; third antennal joint not specially long, but about equal to next two together; facial foveæ broad, entirely dark, separated from eye by a rather wide band, which, however, is not shining; mesothorax dull anteriorly, posteriorly polished, with scattered rather small punctures; scutellum shining; area of metathorax poorly defined, triangular, entirely dull, weakly plicatulate at base; mesopleura moderately glistening. Wings long, brownish hyaline, more dusky at apex; stigma moderate, black; nervures dark fuscous; basal nervure meeting nervulus; second cubital cell broad, receiving recurrent nervure about middle; spurs light reddish. Abdomen shining, very finely but distinctly punctured; second tergite in middle depressed much more than a third but less than a half.

Japan, near Tokyo; on *Azalea*, May 13, 1929 (*Dorsett and Morse*). U.S. National Museum.

A very distinct species, which runs out in my table of Japanese *Andrena* (Ann. & Mag. Nat. Hist., Feb. 1913) next to *A. watasei*, Ckll.

Nomia semiaurea thor, subsp. n.

♀.—Tegument of legs entirely black.

♂.—Described in "Bees.—CXVII.," p. 137.

Thursday Island, March 15 (*Cockerell*).

IX.—*Some Remarks on* Dictyoconoides, *Nuttall* (=Conulites, *Carter* =Rotalia, *Lamarck*). By C. van Rijsinge, The Hague, Holland.

[Plates V. & VI.]

In 1861 H. J. Carter created for some conical fossil Foraminifera the new genus *Conulites*, of which he described one species: *Conulites cooki* (H. J. Carter, "On Fossil Foraminifera of Scinde," Ann. & Mag. Nat. Hist. ser. 3, vol. viii. 1861, pp. 331–332, and pp. 457–458, pl. xv. figs. 7 *a–g*).

The next year W. B. Carpenter, having examined the new-described forms, came to the conclusion that he could best unite this genus and *Orbitolina*, d'Orbigny, with the genus *Patellina*, Williamson, and hence in his 'Introduction' the fossil appeared under the name *Patellina cooki* (W. B. Carpenter, W. K. Parker, and T. R. Jones, 'Introduction to the Study of Foraminifera,' 1862, pp. 233–234, text-fig. xxxviii. *a–g*).

In 1905 H. Douvillé and Ch. Schlumberger referred briefly at the end of a publication on *Dictyoconus* and *Lituonella* to the genus *Conulites*, Carter, stating:—"Il résulte en tout cas de ces indications que ce genre appartient aux Perforés" (H. Douvillé and Ch. Schlumberger, "Sur deux foraminifères éocènes," Bull. de la Soc. géol. de France, ser. 4, pt. v. 1905, p. 304).

This is a most important remark, that apparently has been overlooked, as we find the genus *Dictyoconoides* placed by Cushman in his last classification in the family of the Orbitolinidæ, which contains only imperforate forms, with mostly arenaceous tests.

There are not many studies of the subject until the publication of W. L. F. Nuttall in 1925 *; they are of no importance, or maybe I have overlooked them.

The name *Conulites* according to his investigations being preoccupied, he proposes the name *Dictyoconoides*, as externally Carter's *Conulites* is somewhat like *Dictyoconus*.

He states that the fossil, described by Carter as *Conulites*, cannot be arranged in the group of *Patellina*, as Carpenter did, for the following reasons:—

1. There being no segmental arrangement of the chambers.

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* W. L. F. Nuttall, "Two Species of Eocene Foraminifera from India," Ann. & Mag. Nat. Hist. ser. 9, vol. xvi. 1925, p. 370.

2. The genus *Patellina* not having, in its original description, the internal pillar-structure, which is one of the peculiar characteristics of *Dictyoconoides*.
3. *Patellina* being much smaller than the now-called *Dictyoconoides* *.

The only resemblance is the conical shape, but it is really impossible to consider this as a proof of the relation between these forms, since a conical outline is found also in other Foraminifera and may be regarded as an adaptation to the life-circumstances of the animal.

There are also marked differences between *Dictyoconus* and *Dictyoconoides* :—

1. *Dictyoconus* being arenaceous, while *Dictyoconoides* is calcareous.
2. *Dictyoconus* having a subepidermical reticulate structure.
3. The central part (umbilicus) of *Dictyoconus* being filled up with chambers and not with pillars, as is the case in *Dictyoconoides*.

Thirdly, Nuttall demonstrates the difference between *Dictyoconoides* and *Orbitolina* :—

1. *Orbitolina* being arenaceous.
2. The chamber-arrangement of *Orbitolina* being cyclical and not spiral.

Supposing that the description given by Carter is not complete, Nuttall gives another description of *Dictyoconoides cooki*, from which it may be well to refer to some points.

A remarkable fact is that all the tests examined by Nuttall happened to be microspherical. The septal partitions between the chambers were double, just as is the case in *Nummulites*; they showed canals, whose further extensions, however, could not be traced. Seen on a transverse slide the chambers open at the ventral side towards the umbilicus. These internal openings "represent cells, which are divided by horizontal partitions."

Vertically these "cells" are divided by columns, which radiate first from the apex, later on from the whorl-walls. They show fine longitudinal striations. They do not enlarge near the end. Nuttall states that there is not a trace of a lateral communication between the chambers.

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* Hofker tells me that he has discovered in *Patellina* the typical inner characteristics of *Rotalia*. Publication of these views will follow soon. As I also, as will be shown, could trace the close relation of *Dictyoconoides* to *Rotalia*, it was after all not so wrong to consider those two genera as a single genus.

H. Douvillé published in 1926: "La Forme conique chez les Foraminifères et le genre *Dictyoconoides*, Nuttall" (Bull. de la Soc. géol. de France, ser. 4, part xxvi. 1926).

In this study Douvillé refers to the conical shape as being a result of the surroundings of the individual, the quantities of food, and a pre-existing deformation of the initial chamber. He also mentions the intercalary spirals, which he supposes are formed when the last chamber before the bifurcation has two apertures instead of one. The columns bear at more or less regular distances apophyses, which correspond with the periods of growth of the organism.

The lacunæ thus remaining between those columns and apophysis must—according to Douvillé—have been filled up with protoplasm and are connected by means of lateral openings with the interior of the chambers in the whorl.

The walls of the test are finely porous, which is—as Douvillé emphatically declares—different from *Dictyoconus* and *Orbitolina*, these genera having an arenaceous test.

The same year (1926) brings also an elaborate study by L. M. Davies: "Remarks on Carter's Genus *Conulites* (=*Dictyoconoides*, Nuttall), with Description of some new Species from the Eocene of North-west India" ('Records of the Geological Survey of India,' vol. lix, part 2, p. 237).

He recalls that Wynne (Mem. Geol. Survey of India, vol. xi. part 2, p. 139) described some Rotalinæ from the Eocene, between which—as he thinks—this *Dictyoconoides* can also be found.

Yet Davies is here referring to *Conulites* and maintains this name in his article for the new species there described. I believe, however, that it is not right to keep the name *Conulites* for these Foraminifera, the name being used too much for other organisms.

So I think it best to replace this name by the name *Dictyoconoides*, Nuttall *.

Now Davies describes *Conulites kohaticus*, and here he states that he could not clearly distinguish the embryonic chamber, and thus was unable to state dimorphism.

He mentions *D. kohaticus*, var. *spintangiensis*, a flatter, somewhat larger, and more heavily built variety, *D. kohaticus*, var. *blanfordi*, a more conical form, *D. vredenburgi*, a rather small form, with relatively large chambers, and *D. tipperi*, a little globular Foraminifer, with enormous chambers.

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* As I will show later, I consider *Dictyoconoides* to be a typical *Rotalia*. To prevent confusion, I thought it better to retain in this article the name *Dictyoconoides*.

In 1928 appeared a study of H. Douvillé, wherein he suggested that the genus is referable to the same family as *Calcarina* (Séances de la Soc. Géol. de France, Compte rendu sommaire de 2 avril 1928, p. 94).

As I have not been able to obtain this article, I am sorry I am unable to refer its contents.

The study of *Dictyoconoides* had progressed so far when in two letters L. M. Davies questioned J. Hofker about the problem and also sent some material.

Dr. Hofker kindly transferred the material to me, who am at present studying Foraminifera in his laboratory. I wish to express here my special thanks to him for his calling my attention to these interesting fossils, and also for the kind and valuable advice he gave me during the study of *Dictyoconoides*.

To complete my study of the literature I may append here the ideas of L. M. Davies expressed in his letters of 30 April and 24 June of 1928, just mentioned.

Here Davies calls the type rotaliform, but states that there is some conformity with the Nummulites and Orbitoids :—

1. The presence of pillars.
2. Traces of a supra-cortical skin that can be found on the upper surface.
3. The spiral, which may be left- as well as right-handed, this being in his estimation an indication of bilateral symmetrical inclination.

However, there is some difference :—

In Nummulites: there being no marginal cord.

In Orbitoids: the spiral arrangement of the chambers, as they are arranged cyclically in the Orbitoid species.

The septa seem to be perforated at the base and the chambers open in the umbilicus.

In his second letter he refers to the above-mentioned study of H. Douvillé (1928) and sets out the differences from *Calcarina* according to him :—

1. The typical spines of this genus are never found in *Dictyoconoides*.
2. The pores of *Dictyoconoides* are finer than those of *Calcarina* and never coalesce.

3. In *Calcarina* there are never the intercalary spirals which are so common in *Dictyoconoides.*
4. The communication between the chambers of *Dictyoconoides* is formed by one single large perforation.

Dictyoconoides has so far been found only in the Lower and Middle Eocene of North-west India, the Eocene of South Arabia, the Middle Eocene of Northern Somaliland.

Finally, Davies remarks: "I am struck by the apparent bilateral characters of this genus, as well as by its apparent affiliations to *Rotalia.*"

In short, with respect to the relationships of *Dictyoconoides,* we must decide between *Rotalia, Calcarina, Nummulites, Orbitoides,* and *Orbitolina,* these names being already mentioned in literature, or perhaps establish quite another relationship.

It is possible to divide the above-mentioned Foraminifera into two groups. As the Calcarines, Nummulites, and Rotalids are more closely allied, they can be separated from the Orbitolines, which are in no respect related to the first-mentioned three groups, and the Orbitoids, which also are not so closely allied to the first three.

In the most modern work on the classification of Foraminifera (J. A. Cushman, "Foraminifera, their Classification and Economic Use," Cushman Laboratory for Foram. Research, Special Publication No. 1, Sharon, Mass., 1928, p. 178) the family Orbitolinidæ is said to have the following characteristics :—"Test usually conical; early chambers spiral, later ones annular, subdivided into chamberlets, the central portion of the test with irregular chambers; wall finely arenaceous, siliceous, or calcareous; apertures on basal side of the test multiple in higher forms."

As will be shown, there are really great differences between the hitherto-known species of *Dictyoconoides* and the definition of the family Orbitolinidæ just given.

There is no question about the whorl of chambers in later periods of life becoming cyclically arranged, nor can anything be found that indicates a subdivision of the later chambers into chamberlets. Also, it is wrong to suppose the inner structure of the test to be built up by irregular chambers. As Douvillé (H. Douvillé, *l. c.* 1926, p. 25) has already declared, the walls of the test are finely porous, which indeed marks a great difference from the imperforate family of Orbitolines. Nor can it be denied that there are *not* many apertures on the basal side of the test. Probably

Cushman means the openings of the umbilical canal-system at the basal side, when referring to "apertures."

Thus it will be clear that *Dictyoconoides*, having only its systematically unimportant conical shape in common with the Orbitolines, must be removed from this family.

The differences did not remain unobserved by Cushman, who declared in his work cited above (J. A. Cushman, *l.c.* 1928, p. 184):—"*Dictyoconoides* is a very peculiar form, and probably has its affinities with the Rotalidæ or related families, but is left here until more is known of its relationships."

The Orbitoididæ are as yet not a quite logically arranged family, systematically speaking, as Wayland Vaughan points out in Cushman's "Classification" (J. A. Cushman, *l.c.* 1928, p. 335). This definition of the family is as follows:—

"Test thin or inflated, round lenticular, selliform or stellate, with a layer of equatorial chambers, which in the megalospheric generation begins growth from a multilocular embryonic apparatus. Chamber-walls perforate, usually also communication between chambers through openings for the passage of protoplasmatic stolons. *There is no canal-system.*"

As published sections and my own preparations show, there is no question about the growth from a "multilocular embryonic apparatus." Also the chambers are not equatorially arranged. Finally, of great importance is the absence of a canal-system in Orbitoids, as a canal-system is markedly and typically developed in *Dictyoconoides* and places it near the rotaliform Foraminifera. Coming now to Rotaliidæ, Calcarinidæ, and Nummulitidæ, it is perhaps best to give an account of the characteristics, place, and composition of these families.

It is a remarkable fact that, until now, most of the characters used for the limitation of families, genera, and species are taken from the general habitus of the animals. Nor can it be gainsaid, that, so long as, by a deeper study, important differences in internal structure are not known, one has a right to describe the very same forms by the same name, and, on the other hand, forms in shape widely apart by different generic and family names.

However, there can be found many evidences in foraminiferal literature that the outer shape is not a safe guide for the determination of relationships.

So we may perhaps as well, or better, turn our attention to the internal structure of the Foraminifera. As an account of this subject will fully agree with the views of Hofker, I might perhaps refer to his work on the 'Siboga' Foraminifera (J. Hofker, "The Foraminifera of the 'Siboga' Expedition," Monograph iv. of 'Uitkomsten op Zoologisch, Botanisch, Oceanographisch en Geologisch Gebied, verzameld in Nederlandsch Oost Indie,' 1899–1900 aan boord van Hr. Ms. 'Siboga.' Edited by Dr. Max Weber, Leiden 1927, part i.) and his study on the Nummulitidæ (J. Höfker, "De Nummulitidæ," Tijdschrift Nederl. Dierk. Vereeniging, (2) part xx. 1927, p. 3), but as the first may not be so easily obtained and the second is written in a little-known language, it will not be superfluous to set out the contents here.

It is possible to distinguish two groups in the genera which so far have been assigned to the family Rotaliidæ when studying the inner structure: one group possessing a remarkable and typical canal-system and one group lacking it. As far as known now, Rotalia alone shows this system.

The family of the Calcarinidæ also shows this characteristic. There are the genera *Calcarina*, *Baculogypsina*, *Arnaudiella*, and *Patellispira*, which have a typical Rotalid canal-system, and so all the genera of this family may be regarded as a more or less distinct subfamily in the family Rotaliidæ.

To this family now can also be added the subfamily of the Polystomellidæ, generally considered as a part of the Nummulitidæ.

The Nummulitidæ, too, show a canal system that, though it may possess many resemblances to that of the Rotaliidæ, is distinctly different from it.

The canal-system of the Rotalid forms mentioned above consists of a typical spiral canal, running close under the whorl of chambers. From it spring interseptal canals, which may be simple in lower forms, but in the highest development in their turn give off little branches and in the end open with bifurcations at the dorsal suture of the shell (*cf.* the description of *Dictyoconoides kohaticus*). The spiral canal itself continues to run under the chamber-whorl, and finally opens at the umbilical margin of the last chamber. The chambers show a prolongation towards the ventral side, which in *Rotalia polystomelloides* is prolonged into the septal wall and on the other side opens in the spiral canal (J. Hofker, "Foraminifera of the 'Siboga' Expedition," part i. 1927, p. 35, pl. xvi. figs. 2, 4, and 5).

From the spiral canal canals branch off also towards the umbilicus. In *Rotalia polystomelloides* they run straight on to the ventral side and there they open. In *Rotalia schroeteriana* they form an irregular network and also open on the ventral side of the shell in the umbilical region (J. Hofker, *l. c.* 1927, pl. xix. figs. 8 and 9).

This system is also typically shown in the Calcarinidæ and the Polystomellidæ. In the latter the system is double, as there is an umbilicus at both sides of the test.

The family of the Rotaliidæ thus includes the subfamilies Rotaliinæ, Calcarininæ, and Polystomellinæ.

In the Nummulitidæ it is possible to separate a primary and secondary canal-system. The primary canals are formed in *a single* chamber-wall, really as a canal. The secondary canals are formed when two chamber-walls meet, grow together, and some space is left between them. (In this way the Rotalid system is formed.) The primary canal-system is to be found at the marginal side of the chambers. In the first rows it forms a simple canal, but later on by anastomosing the "marginal cord" is formed. From this marginal cord there extend many canals mostly secondarily formed. So there is really a pronounced difference from the Rotalid spiral system, this being formed secondarily at the base of the chambers and extending along the umbilical side.

The Nummulitidæ have an embryonic structure that in the megalospheric forms does not show a so-called "raspberry-structure," like the Planorbulinidæ, which, moreover, do not possess a canal-system.

Thus defined, the true Nummulites are: — *Assilina, Nummulites, Operculina, Heterostegina, Spiroclypeus, Cycloclypeus* (J. Hofker, "De Nummulitidæ," Tijdschr. Nederl. Dierk. Vereen. (2) pt. xx. 1927, p. 3).

DESCRIPTION OF THE MATERIAL.

L. M. Davies kindly sent:—

Dictyoconoides kohaticus, from the uppermost Laki beds of Kohat.

D. kohaticus, from the uppermost Laki beds of Bahadur Khel.

D. kohaticus, var. *spintangiensis*, from Spin Tangi.

D. vredenburgi, from the middle Laki beds near Hindu Bagh.

D. haimei, from the uppermost Ranikot beds at Thal.

For this beautiful material we are greatly indebted to him, and now express to him our best thanks.

According to L. M. Davies the geological succession is as follows :—

Lutetian	Khirthar.
Ypresian	Laki. Uppermost Ranikot.
Landenian	Ranikot.

(L. M. Davies, "Notes on the Correlation of Pinfold's Chharat Series with the Eocene Stages of Sind and Europe," Transact. of the Mining & Geol. Inst. of India, part 3, 1926, p. 195.)

In his letter of 24 June, 1928, Davies evidently regards the uppermost Ranikot as also Landenian, since he places *Dictyoconoides haimei* and other types of the Ranikot and uppermost Ranikot altogether in the Landenian.

It may be remarked that the terms Landenian and Ypresian are not always used, and by E. Haug they are included to the Londinian (E. Haug, 'Traité de Géologie,' part ii. fasc. 3, pp. 1424, 1419). Also Haug does not refer the Londinian to the Eocene (as Davies and others do Landenian and Ypresian), but to the Palæocene.

Dictyoconoides kohaticus, Davies. (Pl. VI. figs. 1–4.)

Conulites kohaticus, Davies (L. M. Davies, "Remarks on Carter's Genus *Conulites* etc.," Rec. Geol. Survey of India, vol. lix. part 2, 1926, p. 240, pl. xvi. figs. 1–4, pl. xvii. figs. 5–5 *c*).

Conulites kohaticus, var. *spintangiensis*, Davies (L. M. Davies, *l. c.* p. 245, pl. xvii. fig. 6).

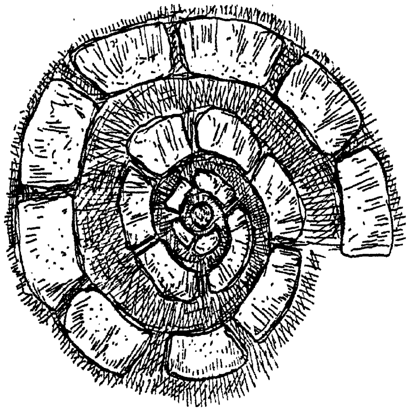
The sample contained three distinctly different types, though it was quite obvious that they must belong to the same species, their only difference being the more or less conical shape and (as will be shown further on) the dimensions of their embryonic chamber.

One type was a rather high conical form, having a basal diameter of about 5 mm. and a conical height of 2 mm. (Pl. VI. figs. 4 *a*, *b*). A slide made through the embryonic apparatus showed a large first chamber (text-fig. 1).

The second type also was rather conically shaped, though much less than the first. The basal diameter was about 7 mm. and the conical height 2 mm. or little less (Pl. VI. figs. 3 *a*, *b*). The slide showed beyond doubt that the form was a megalosphericone (text-fig. 4).

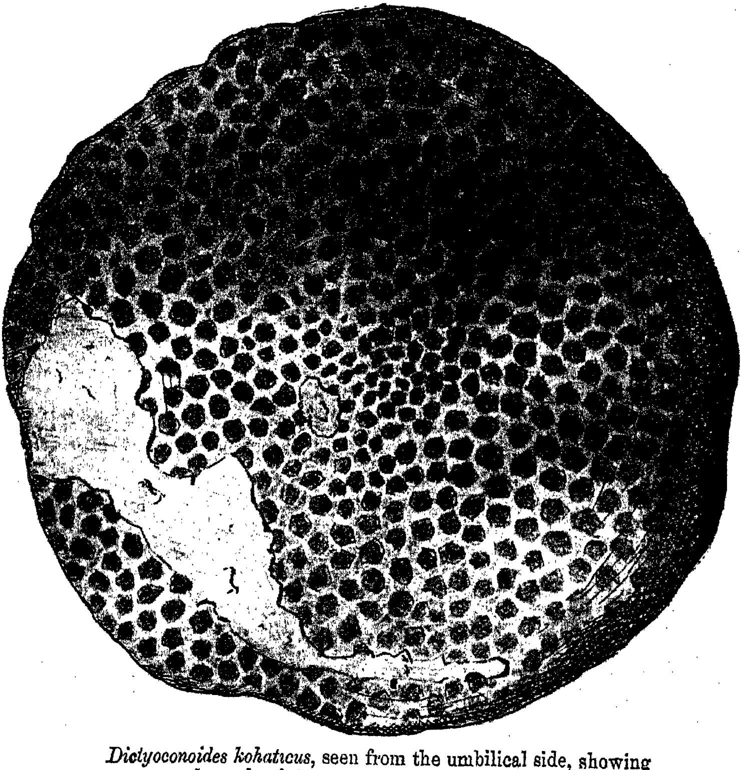
The third form is a much more flattened type of 8 and more mm. basal diameter, while the conical height never attained 2 mm. and usually was about 1 mm. (Pl. VI. figs. 2 *a*, *b*).

Text-fig. 1.



Dictyoconoides kohaticus. Cross-section through the embryonic apparatus. Megalospheric type. × 80.

Text-fig. 2.

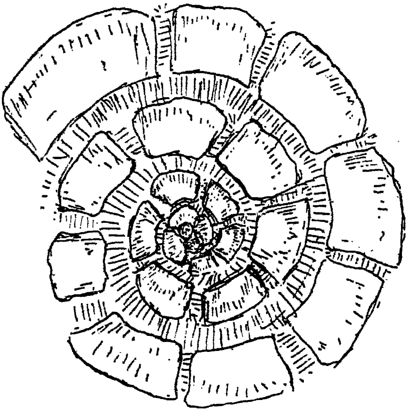


Dictyoconoides kohaticus, seen from the umbilical side, showing the ends of the umbilical "pillars." × 15.

The section, horizontally through the embryonic apparatus, showed a microspheric first chamber (text-fig. 3).

It was not always easy to decide whether an individual belonged to the effilated or the flattened conical type. But that does not appear to be astonishing, for if Hofker's ideas about the subject are correct, there must needs be a large series of individuals, which, although belonging to the megalospheric generations, show more or less slight gradations and variations towards the microspheric type.

Text-fig. 3.



Dictyoconoides kohaticus. Cross-section of the microspheric embryonic apparatus. × 80.

But they are always distinctly separated from the true microspheric generation. In a hundred specimens of *Dictyoconoides kohaticus* there were nine microspheric individuals, seven megalospheric high conical and eighty-four megalospheric lower conical individuals—an abundance of the intermediate megalospheric form that might be expected on the theory of heterogamy (trimorphism).

With regard to the description of the outer habitus of the species, I may refer to the original description of Davies (L. M. Davies, " Remarks etc.," *l. c.* 1926, p. 241).

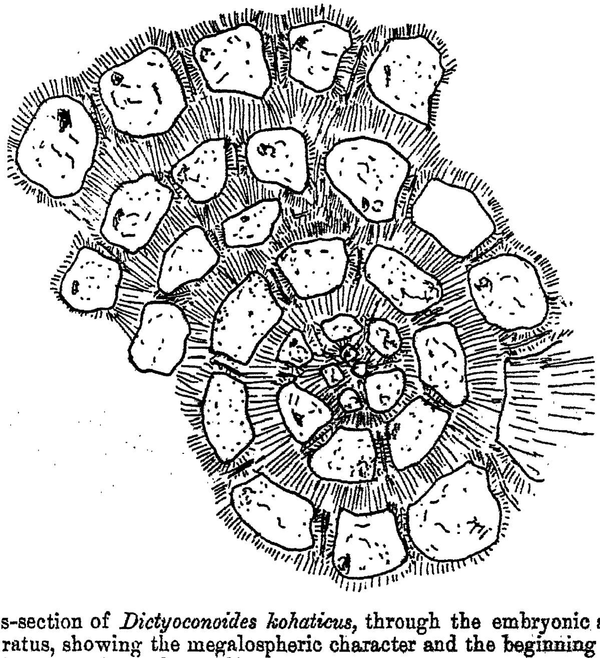
In horizontal section, the figure one can see is different, according to the height of the section.

The upper section shows the initial chamber and the first whorls of the chamber-spiral. The megalospheric individuals (text-figs. 1, 4) show distinctly a first chamber, followed by the rest of the chambers, which are all to be seen apart. The microspheric ones (text-fig. 3) show an initial chamber, with a first row of partly underlying, though spirally ranged, following chambers (the apparent disorder of the first four or five chambers does not form a "raspberry-apparatus," as is, for instance, the case in the Planorbulinidæ).

It is obvious that in the microspheric forms the first whorls show chamberlets of a much smaller size than the equivalent chambers of the megalospheric forms.

The walls are calcareous and distinctly, though finely, porous, and the septa between the chambers are penetrated by a canal, or rather (though this cannot be seen in a horizontal section) by a system of canals.

Text-fig. 4.

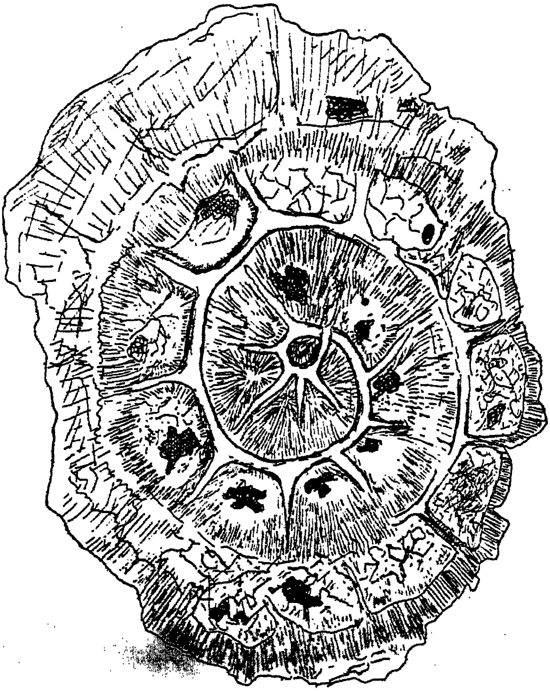


Cross-section of *Dictyoconoides kohaticus,* through the embryonic apparatus, showing the megalospheric character and the beginning of an intercalary whorl. × 60.

The origin of those canals is to be seen in a section cut immediately under the first whorls (text-fig. 5). There appears a beautiful spiral canal formed quite like that figured by Hofker in his work on the 'Siboga' Foraminifera (J. Hofker, "The Foraminifera of the 'Siboga' Expedition," *l. c.* pl. xix. figs. 12, 9, 4, and others). It branches off between the chambers.

As all the examined *Dictyoconoides* are fossilised specimens and during the fossilisation were totally filled up with calcite, it is not possible to apply here the "canada-balsam method" of Hofker. But in his habitus the spiral canal of *Dictyoconoides kohaticus* resembles perfectly that of *Rotalia schroeteriana* and *R. polystomelloides*, which are looked upon by Hofker as possessing a typically Rotalid canal-system. As in the forms here mentioned, the spiral canal runs on the umbilical side of the spiral of chambers, quite near to the chambers themselves. Besides, I could observe (near A in text-fig. 7) a bifurcating end of an interseptal canal. Here and there it was quite possible to observe the interseptal canals giving off their branches (text-fig. 6). So it does not appear unreasonable to conclude that the spiral canal-system is quite on the plan indicated in plate xix. fig. 4 of the already-mentioned 'Siboga' work of Hofker.

Text-fig. 5.



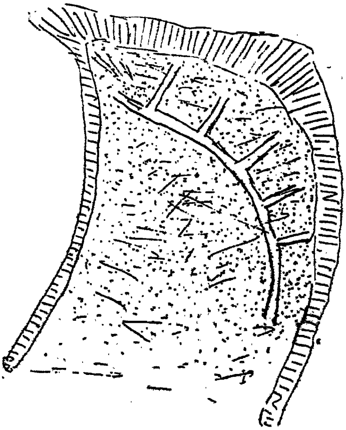
Cross-section of *Dictyoconoides kohaticus* just below the embryonic apparatus, showing the typical Rotalid spiral canal. × 60.

A yet lower cut section may reveal the secret of the structure of the umbilical canal-system, but, as I could better trace this in *Dictyoconoides vredenburgi*, I postpone the discussion of it until I describe that species.

A section not high above the base shows some spiral rings of chambers and cross-sections of the "columns" and interlocated "chamberlets" that form part of the umbilical system. I also postpone their interpretation till the discussion of *Dictyoconoides vredenburgi*.

A transverse section through the initial chamber (text-fig. 7) shows a cross-section of the chamber-spiral covered towards the outer whorl with a—near the top thickest—layer of finely perforated chalk-material, which bears here and there little outgrowths, in which one can now and then detect a bifurcation of the interseptal canal. Those granulations are not regularly spread, but generally they are more closely packed in the upper region.

Text-fig. 6.



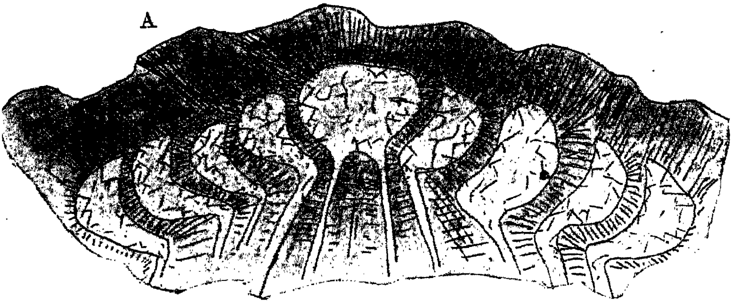
Section through septum, showing an interseptal canal with branches. × 180.

The chambers open at the base towards the umbilical region (text-fig. 8). From every chamber-wall emerges a basally directed pillar-shaped prolongation and a more horizontally directed wall. They are placed almost vertically to each other, and so the transverse section gives the impression of a chamber-filled umbilical region.

Yet by thoroughly studying, comparing, and combining horizontal and vertical sections, it must become clear that there can only be recognised a system of canals (umbilical canal-system) which are connected with the inner contents of the chambers. So I must decidedly oppose the opinion of Davies and other authors, who speak about the openings as "secondary chambers."

It is not easy to indicate on the transverse sections where the spiral canal has been cut, but that is not so strange, owing to the trifling width of the canal and the complete calcifying of the test.

Text-fig. 7.



Dictyoconoides kohaticus. Transversal section through the top, showing some chambers and a part of the umbilical region. Also the umbilical opening of the chambers and the upper part of the "pillars" are to be seen, as well as the thickness of the calcareous skin, with its granulations. Near A can be observed that canals end in those granulations. × 60.

As to the variety *spintangiensis*, I can see no clear difference between it and the microspheric form of *Dictyoconoides kohaticus.* Indeed, there are individuals of *D. kohaticus* and of the variety *spintangiensis*, both from the collection of Davies, which I cannot possibly distinguish from each other.

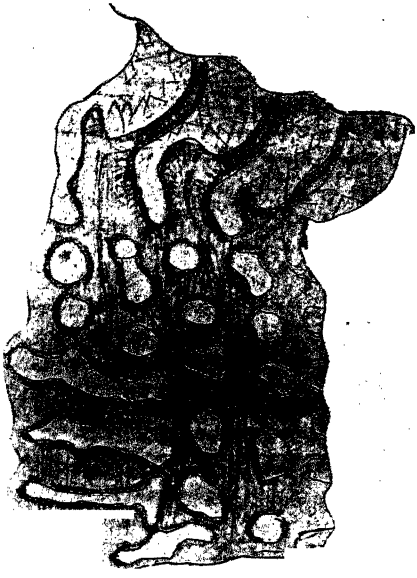
The differences which guided Davies in his creating the new species were (1) its being bigger, (2) its being flatter, than the normal type.

Davies adds: "This appearance of flatness is due to the thickening and turning upwards of the outer rim of the test."

It appears to me that these differences are not of so great an importance, as they show every gradation to the original species, and may not always be distinguishable from it with certainty.

Now, it is an essential fact, stated by Davies, that the variety *spintangiensis* always occurs with the original *Dictyoconoides kohaticus,* but is found in larger quantities in the southern parts of the district where *kohaticus* is found. He adds in an important note: "It is noticeable, though, that the specimens from Lower Sind, still further south, often approximate to the normal *kohaticus* type, rather than to the *spintangiensis* variety" (L. M. Davies, "Remarks etc.," 1926, *l. c.* p. 245).

Text-fig. 8.



Transversal section through *Dictyoconoides kohaticus* (part), showing part of the umbilical system and chambers. In the vertical "pillars" canals are running. × 60.

A remarkable fact, shown by sections of the variety *spintangiensis,* is that these forms are all microspheric, and there are no megalospheric specimens as would be expected if the variety *spintangiensis* really was a variety.

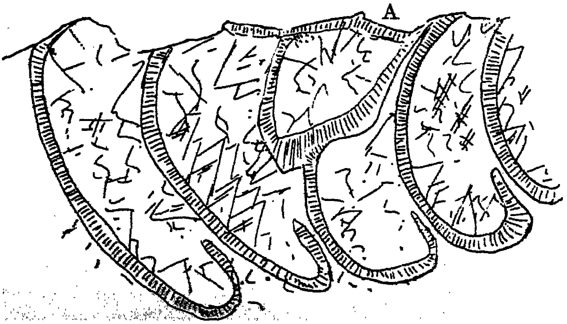
Besides the Spintangi-zone, where the variety has been found in larger quantities, has some peculiarities, so that it usually is placed in the lower Khirthar, which immediately follows the Laki-series. Davies is inclined to determine the strata as a *special facies* of the uppermost Laki and basal Khirthar series.

So, on the whole, I am inclined to consider *Dictyoconoides kohaticus*, var. *spintangiensis*, Davies, as a microspheric *Dictyoconoides kohaticus*, Davies, that may perhaps in the special life-circumstances of the Spintangi-facies have developed some deviating qualities in outer shape.

I could not quite make out the difference between *D. kohaticus* and *D.* (*Conulites*) *cooki*, Carter. It seems that Davies also had some doubts as to the difference between those two species (L. M. Davies, " Remarks etc.," 1926, *l. c.* pp. 243–244). Davies tried to check his opinion by studying the type-specimens of Carter, but they proved to be lost. So he could not confirm his opinion in this way.

Of course, I cannot decide here, but I should not be much surprised if *Dictyoconoides cooki*, Carter, proved to be nothing else than the megalospheric high conical form of *D. kohaticus*, Davies. But as long as there is no actual proof of this surmise, we must distinguish the two species.

Text-fig. 9.



Dictyoconoides vredenburgi. Transversal section, shewing some of the chambers, with their openings towards the umbilicus and near A the beginning of an intercalary whorl. The chambers are filled up with calcite crystals. × 80.

Dictyoconoides vredenburgi, Davies.

Conulites vredenburgi, Davies (L. M. Davies, " Remarks on Carter's Genus *Conulites* etc.," Records of the Geol. Survey of India, vol. lix. part 2, 1926, p. 246, pl. xvii. figs. 7–7 *b*).

Davies says about this species that it differs specifically from *D. kohaticus*. " It is a relatively small flat form, with cortical chambers so large in proportion to the test as a whole, as to constitute in my opinion a specific difference in type " (L. M. Davies, " Remarks," 1926, *l. c.* p. 247).

This is really an obvious difference from *kohaticus*, the more so, since—as Davies also states—there are no gradations between this type and *D. kohaticus*.

It also does not always occur amidst the other Foraminifera; it is found by Davies in one place only.

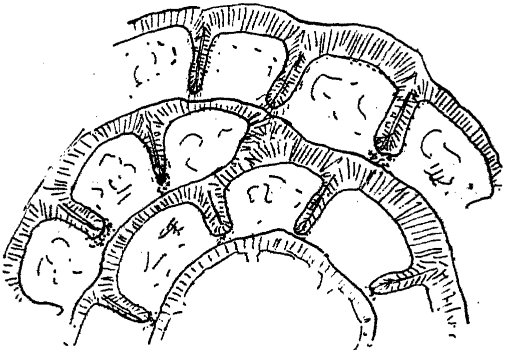
Examining the received sample (altogether six specimens) it was possible to distinguish a flat and a more conical type, and a slide demonstrated that the flat individual belonged to the microspheric generation, the more conical to a megalospheric one.

For these reasons I quite agree with Davies in considering it as a species different from *kohaticus.*

The inner structure—except the bigness of the chambers—did not demonstrate any difference from that of *Dictyoconoides kohaticus.* Here also the spiral canal could be traced in its typical Rotalid development.

A transverse section showed the structure known already from *D. kohaticus.* Only the connection of the chamber-contents with the umbilical canal-system was very clearly demonstrated here (figs. 8, 9). One wall strongly curves to the umbilical side and runs a little distance upward, parallel to another wall. Through the opening thus formed between them the communication is created. Also two "pillars" of calcareous material run, one vertically, the other more horizontally, which border a system of openings, the umbilical canal-system, that by the fore-mentioned ventral opening communicates with the chamber. In this transverse section, too, it is difficult to indicate where the spiral canal runs. In horizontal section it runs beneath the marginal walls between two whorls (cf. *Rotalia schroeteriana*).

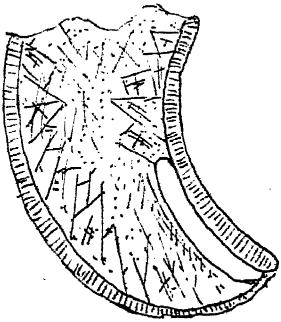
Text-fig. 10.



Cross-section showing the connection of the chambers by the apertures and the beginning of an intercalary whorl. × 80.

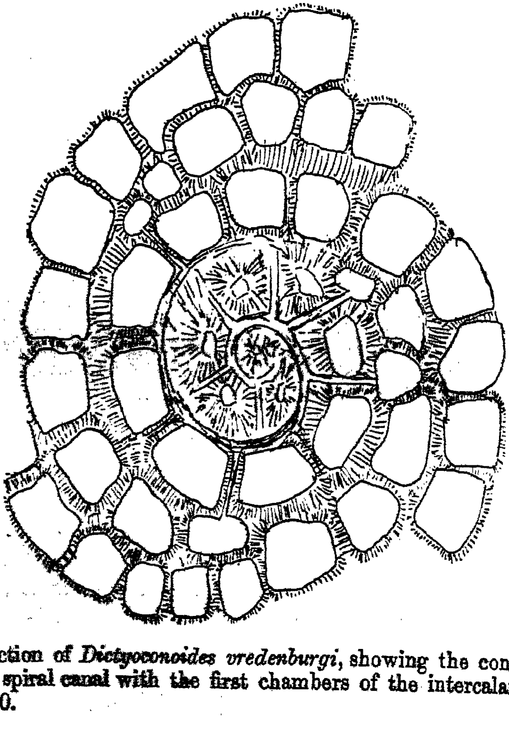
Pl. V. shows a reconstruction of a part of a *Dictyoconoides vredenburgi.* It does not greatly differ from *D. kohaticus.*

Text-fig. 11.



Section through septum, showing the aperture. × 120.

Text-fig. 12.



Cross-section of *Dictyoconoides vredenburgi*, showing the connection of the spiral canal with the first chambers of the intercalary whorls. × 60.

In one horizontal slide I thought I could—though not with the greatest certainty—see something of the genesis of the intercalary whorls (text-figs. 9, 10, and 12).

One of the branches of the spiral canal—an interseptal one—seemed to pass straight on to the first chamber of the intercalary whorl wherein it opened.

In the cross-section here published (text-fig. 12) there is one place in the regular arrangement of the chambers where it seems that two chambers struggle for a place in the spiral, one lower, the other higher. The interpretation may be that—by what cause is not clear—a chamber is formed at the end of the branch of the spiral canal near the last chamber of the existing whorl. The forming of the first intercalary chamber and a new chamber of the original spiral are simultaneous and one chamber displaces the other. In the forming of the next two chambers this process is continued, and so, finally, the intercalary whorl has assumed its place amidst the original ones. I should not like this to be considered a certainty, but I give it as a possibility that, in my opinion, has some probability.

Conclusions.

We can gather the following facts from the notes given above:—

1. Hitherto especially the outer shape has been used to classify *Dictyoconoides*.
2. *Dictyoconoides* possesses a typical Rotalid canal-system, *i. e.*, a spiral canal, with branches towards the umbilicus and in the septa. The branches in the septa bifurcate in many places and the branches in the umbilicus are part of the "umbilical canal-system" that corresponds with the chambers.
3. *Dictyoconoides* also shows other Rotalid characteristics: a spiral of chambers, conical shape, finely perforate walls, a closed umbilicus.
4. So *Dictyoconoides* must be considered to be a Rotalid.
5. The above-mentioned characteristics classify *Dictyoconoides* as a typical *Rotalia*.
6. The name *Dictyoconoides* is to be replaced by the name *Rotalia*.
7. *Rotalia kohaticus*, Davies, typically shows *trimorphism*.

EXPLANATION OF THE PLATES.

Plate V.

Reconstruction of a part of *Dictyoconoides*.

Plate VI.

Dictyoconoides kohaticus, Davies.

X.—*New or little-known* Tipulidæ (*Diptera*).—XLIV. *Australasian Species.* By Charles P. Alexander, Ph.D., F.E.S., Massachusetts Agricultural College, Amherst, Massachusetts, U.S.A.

The crane-flies discussed in this paper are from Queensland, New South Wales, Victoria, and West Australia, and were collected by my friends Messrs. Clark, Davidson, Dodd, Ferguson, Heron, Mathews, Perkins, Taylor, and Wilson, to whom my deepest thanks are extended. Where not indicated to the contrary, the types of the novelties are preserved in my collection.

Dolichopeza (*Dolichopeza*) *illingworthi*, sp. n.

Thorax almost uniform fulvous-yellow, the pleura paler yellow; legs brown, the genua scarcely brightened; posterior tibiæ broadly white at tips; fore and middle basitarsi brown, the tips white; posterior basitarsi pure white; wings whitish subhyaline, the apex and a narrow seam on anterior cord dark brown; abdominal segments black, ringed at near mid-length with ochreous.

Male.—Length about 7·5 mm.; wing 7–7·5 mm.

Frontal prolongation of head obscure yellow, the palpi dark brown. Antennæ (♂) of moderate length, if bent backward extending to beyond the base of the abdomen; scapal segments obscure yellow, the flagellum dark brown. Head dark brown, the anterior portion more brownish yellow.

Thorax almost uniform fulvous-yellow, the mesonotum immaculate, the pleura clear yellow, palest ventrally. Halteres elongate, pale brown, the knobs dark brown. Legs with the coxæ and trochanters pale brown; femora brown, the bases paler, the genua scarcely brightened; tibiæ dark brown, the distal third of posterior tibiæ snowy white; basitarsi dark brown, the tips and remainder of tarsi snowy white; on posterior legs the tarsi are uniformly whitened. Wings whitish hyaline, the apex narrowly dark brown; stigma and a narrow seam on anterior cord dark brown; veins brownish black. Venation: cells of medial field relatively shallow; *m–cu* nearly its own length before fork of *M*; cell *2nd A* very narrow on basal half, the outer half more expanded to form a weak anal angle.

Abdomen black, the segments ringed with ochreous at or beyond mid-length; hypopygium chiefly ochreous, relatively large. Male hypopygium with the tergite nearly transverse, with an acute spine on either side, the space between nearly transverse, in its median portion produced caudad into a low transverse median lobe. Outer dististyle toothed on mesal face shortly before apex.

Hab. North Queensland.

Holotype, ♂, Kuranda, Cairns District, altitude 1100 feet, on window, March 1921 (*A. P. Dodd*).

Paratopotype, ♂.

I take great pleasure in naming this interesting species in honour of Dr. James F. Illingworth, to whom I am indebted for many Tipulidæ from the Cairns District. The species is allied to *D. varipes*, Skuse, differing especially in the details of coloration and structure of the male hypopygium.

Dolichopeza (*Dolichopeza*) *davidsoni*, sp. n.

General coloration dark brown; pleura pale yellow, variegated with dark brown; legs brown, the femoral tips, tibial bases and tips, extreme proximal ends of basitarsi, and the outer tarsal segments white; wings greyish, the apex and veins beyond cord conspicuously infumed; abdominal tergites dark brown, the outer sternites ringed with yellow.

Male.—Length about 6·5 mm.; wing 7·2–7·4 mm.

Female.—Length about 8 mm.; wing 7·7 mm.

Frontal prolongation of head brownish yellow, dark brown ventrally; palpi dark brown. Antennæ with the scape and basal segments of flagellum pale yellow, the outer segments dark. Head brown, with a sparse grey pruinosity, the anterior vertex and front restrictedly light yellow.

Pronotum light yellow, the cervical sclerites dark brown. Mesonotal præscutum dark brown, the usual stripes scarcely evident, confluent, the humeral region restrictedly light yellow; scutal lobes dark brown, the median region very restrictedly pale; scutellum and postnotum uniformly brown. Pleura pale yellow, conspicuously variegated with dark brown, this including the anepisternum, together with the dorso-pleural region immediately dorsad of it, the ventral sternopleurite, and the meron. Halteres elongate, pale, the knobs dark brown. Legs with the coxæ and trochanters pale yellow; femora pale basally, deepening into brown outwardly to produce a darker subterminal ring, the tips narrowly whitened; tibiæ dark brown, the bases narrowly whitened, the tips broadly pure white; proximal ends of basitarsi more or less whitened, especially evident on the type, where on the hind legs it includes an area only slightly less than the tibial apex; remainder of basitarsi dark brown, the tips and tarsal segments 2 to 4 white; terminal segment infuscated. Wings with a greyish tinge, cells *C* and *Sc* a little darker; stigma elongate, dark brown; wing-apex broadly infumed, connected by broad seams along the veins with a large seam on the anterior cord; medial veins, *m–cu*, and distal section of Cu_1 similarly seamed; whitish areas before and beyond the stigma; veins dark brown, more cream-coloured in the pre-stigmal pale area. Venation: forks of medial field relatively shallow; *m–cu* more than two-thirds its own length before the fork of *M*; cell *2nd A* narrow.

Abdominal tergites uniformly dark brown; basal sternites pale yellow, narrowly ringed with dark brown; subterminal segments with the caudal margins of the segments yellow, the amount increasing on the outer segments. Ovipositor with the genital shield and basal half of the tergal valves blackened, the tips of the latter and the sternal valves pale yellow.

Hab. South Queensland, New South Wales.

Holotype, ♀, Mt. Tamborine, South Queensland, altitude 2000 feet, November 1928 (*W. H. Davidson*).

Allotype, ♂, Eastern Dorrigo, New South Wales, altitude 2000–3000 feet, February 27, 1929 (*W. Heron*).

Paratypes, ♂ ♀, with the allotype.

The species is named in honour of the collector of the type, Mr. Will H. Davidson. *Dolichopeza davidsoni* is allied to *D. annulipes*, Skuse, differing in the wing-pattern, coloration of the thoracic pleura, and details of the leg-pattern.

Dolichopeza (*Dolichopeza*) *dorrigensis*, sp. n.

General coloration dark brown; thoracic pleura with a broad oblique yellow stripe; legs dark brown, the genua, tips of all tibiæ, proximal ends of all basitarsi, and outer tarsal segments snowy white; wings greyish subhyaline, virtually unmarked except for the stigma; *m–cu* about one-third its length before the fork of *M*; abdominal tergites dark brown, with whitish-yellow lateral spots; sternites whitish yellow, with a median series of brown spots.

Female.—Length about 8 mm.; wing 7·8 mm.

Frontal prolongation of head pale yellow; palpi brown. Antennæ dark brown, including the scape; flagellar segments elongate-cylindrical, the verticils longer than the segments. Head rich cinnamon-brown, the anterior vertex and front light yellow.

Pronotum yellow laterally, narrowly dark brown behind. Mesonotum brown, the humeral region of the præscutum restrictedly pale yellow, the scutal region a little brightened. Pleura obliquely lined with pale yellow and dark brown, the yellow band extending from the humeral region to the posterior coxæ, margined in front by a narrow brown line, margined posteriorly by a somewhat wider line of the same colour; propleura extensively pale yellow. Halteres dusky, the knobs dark brown. Legs with the coxæ pale yellow, the base of the fore coxa darkened; trochanters yellow; femora dusky at base, passing into dark brown, the genua narrowly but conspicuously white; tibiæ dark brown, the tips of all legs conspicuously snowy white, broadest on the hind legs; proximal ends of basitarsi narrowly but conspicuously white, the major portion dark brown, the tips again white; remainder of tarsi white. Wings greyish subhyaline, the stigma conspicuously dark brown; a vague, scarcely indicated brown seam on anterior cord; pale areas before and beyond the stigma scarcely indicated; wing-margin in cell Sc_2 narrowly infumed; veins dark brown. Wing rather conspicuously petiolate. Venation: Sc_1 distinctly preserved; forks of medial field relatively deep; *m–cu* at about one-third its length before the fork of *M*; cell *2nd A* unusually long and narrow.

Abdominal tergites dark brown, each segment with a conspicuous yellow lateral spot on posterior ring; sternites greenish, the median portion extensively yellow, with a conspicuous series of brown markings distributed the entire length; in certain lights the yellow coloration of the abdomen is conspicuously white pruinose. Ovipositor with the valves chiefly yellow; tips of the short sternal valves broadly and conspicuously blackened.

Hab. New South Wales.

Holotype, ♀, Brooklana, East Dorrigo, altitude about 2000 feet, March 3, 1928 (*W. Heron*).

Dolichopeza dorrigensis is allied to *D. annulipes*, Skuse, differing in the details of coloration of the wings, legs, and abdomen.

Macromastix (*Macromastix*) *clitellaria*, sp. n.

General coloration of mesonotal præscutum and scutal lobes polished black (♂), more obscurely darkened (♀); postnotal mediotergite yellowish testaceous, with two black spots on caudal margin; legs long and slender, black, the femoral bases broadly obscure yellow; wings with a strong dusky suffusion, the prearcular region and cells *C* and *Sc* dark brown; base of abdomen (♂) fulvous-yellow, the terminal portion black.

Male.—Length about 11–12 mm.; wing 15 mm.

Female.—Length about 10·5–11 mm.; wing 13·5 mm.

Frontal prolongation of head of moderate length only, a little more than one-half the remainder of head, dark brown, paler at apex; nasus very long and slender, tufted with conspicuous setæ; palpi black. Antennæ short, only about as long as the head excluding the frontal prolongation, apparently only 11-segmented; first scapal segment obscure yellow, darkened dorsally; second scapal segment light yellow; flagellum black, the base of the first segment paler; first flagellar segment subpyriform, the succeeding segments becoming more slender; verticils short and inconspicuous. Head dark brown, the posterior orbits narrowly and irregularly light grey.

Pronotum black, pollinose. Mesonotal præscutum (♂) with an extensive polished black dorsal shield, the narrow lateral margins yellowish-grey pruinose; scutal lobes similarly polished black; median area of scutum, the scutellum, and most of the postnotal mediotergite yellowish testaceous, the caudal margin of the latter with two paired black spots. In the female the polished areas of the male are dull, being covered with a sparse pollen. Pleura heavily light grey pruinose, including the dorso-pleural region; pleurotergite with the dorsal portion pale, pruinose, the ventral portion clearer grey. In the female the dorsal portion of the pleurotergite is glabrous. Halteres brownish yellow, the knobs infuscated. Legs with the coxæ light grey; trochanters obscure yellow; femora chiefly black, their bases broadly obscure yellow, the amount of the latter somewhat more extensive on the middle and posterior femora; remainder of legs black; legs very long and slender, the posterior basitarsi longer than the tibiæ. Wings with a strong dusky suffusion, the stigma and cell Sc_1 more yellowish; prearcular region and cells *C*, *Sc*, and small adjoining cells dark brown; veins black, the obliterative areas relatively restricted; distal end of R_{1+2} entirely pale; *Rs* entirely pale brown, without macrotrichia. Macrotrichia lacking on veins beyond the cord, with the exception of *Sc* and R_1. Venation: R_3 nearly in alignment with R_{2+3}, the latter subequal to *Rs*; cell M_1 deep, the petiole subequal to or longer than *m*; cell *2nd A* very narrow.

Abdomen with the basal segments fulvous-yellow, the distal half or less black, the outermost segments pruinose; sternites similarly coloured; hypopygium entirely dark. In the female the abdominal tergites are very extensively covered with a yellowish-grey pruinosity, only the base of tergite 2 being nitidous; basal sternites more extensively glabrous.

Hab. Victoria.

Holotype, ♂, Bogong High Plains, altitude 5600–6000 feet, January 1928 (*F. E. Wilson*).

Allotopotype, ♀.

Paratopotypes, 2 ♂ ♂.

Type returned to Mr. Wilson.

Macromastix (*Macromastix*) *mathewsi*, sp. n.

Male.—Length 11–14 mm.; wing 13–15 mm.

Female.—Length 8·5–12 mm.; wing 9·5–14 mm.

Allied to *M. constricta*, Skuse (New South Wales), differing especially in the details of coloration and structure.

Frontal prolongation of head a little shorter than in *constricta*, opaque by a conspicuous microscopic yellow pubescence, obscure yellow with a narrow dark brown or black lateral line; nasus shorter; palpi black. Antennæ with the scape yellow, the flagellum entirely black. Head yellowish grey.

Mesonotal præscutum yellowish grey, opaque, with four poorly delimited brownish-grey stripes, the intermediate pair confluent and more greyish behind; scutellum and postnotum with an abundant appressed yellowish pubescence. Pleura conspicuously light grey, including the anepisternum, sternopleurite, and pteropleurite, the pleurotergite abruptly yellowish. Halteres dark brown, the stem paler. Legs with the coxæ greyish, the mid-coxæ more clearly so; trochanters obscure yellow; femora yellow, the tips broadly blackened, this including approximately the distal fourth; tibiæ brownish yellow, the bases very narrowly, the tips broadly blackened; tarsi black; all tarsi relatively short, as in *constricta*. Wings broader than in *constricta*, strongly infumed, the base and costal border darker, but not contrasting so conspicuously with the remainder of the wing. Venation: cell *2nd A* narrow, but still much wider than in *constricta*.

Abdominal tergites (♂) dark brown, the basal segments yellow on lateral margins, this narrowing behind; sternites yellow, the subterminal segments black, sparsely pollinose;

hypopygium pale. In the female the abdomen is heavily pruinose, the lateral margins and ovipositor fulvous.

Hab. West Australia.

Holotype, ♂, South Perth, October 20, 1927 (*W. H. Mathews*).

Allotopotype, ♀, September 22, 1927.

Paratopotypes, numerous ♂ ♀, September 22, 1927; October 20–30, 1927; *paratypes*, ♂ ♀, Redlands, September 11, 1927 (*W. H. Mathews*).

"All caught in my garden on the side of a small hill."

I take great pleasure in naming this species in honour of the collector, Mr. Wallace H. Mathews. Although closely allied to *M. constricta*, the present species is clearly distinct. The most conspicuous differences lie in the frontal prolongation of the head, the wings, and coloration of the male hypopygium.

Macromastix (*Macromastix*) *clarkiana*, sp. n.

Male.—Length about 12–13 mm.; wing 15–16 mm.

Female.—Length about 13 mm.; wing 15 mm.

Closely allied to *M. constricta*, Skuse (New South Wales), agreeing in the general coloration of the body and wings, differing in the details of pattern and structure.

Frontal prolongation of head slender, as in *constricta*, but slightly less constricted before mid-length, chestnut-brown. Antennæ with the scape bright yellow, the flagellum black; flagellar segments beyond the fourth narrowed and shortened, the terminal seven shorter than the preceding four taken together. Two more or less distinct brown spots between the eyes.

Ground-colour of the præscutum yellowish grey, clearer laterally, with four entirely separated brown stripes; scutellum and postnotal mediotergite conspicuously yellow pollinose. Pleura chiefly clear grey. Legs with the femora and tibiæ fulvous, tips broadly blackened; tarsi relatively short, as in *constricta*. Wings with a strong dusky grey ground-colour, the pattern distinct from *constricta*; prearcular region darkened, the costal region rather narrowly of the same colour, the amount decreasing toward the stigma, which is chiefly yellow; in cell *R* only about the basal half of the cell is darkened; no distinct dark seam in cell *M* adjoining vein Cu_1, except at base; cell Cu_1 and adjoining portions of cells *M* and *Cu* conspicuously light cream-yellow; veins dark. Wings broader than in *constricta*, especially in the anal region. Venation: cell *2nd A* narrower than in *mastersi*, but broader than in *constricta*.

Abdomen as in the group, the basal segments yellow, the apex, including hypopygium, black. In the female the abdominal tergites are more greyish, with a broad dark brown sublateral stripe on either side; basal segments laterally and the genital segments fulvous-yellow; sternites yellow, the caudal margins of sternites 5 and 6 light grey. Male hypopygium as in *constricta*, but inner dististyle, at base of the elongate rod-like extension, provided only with setæ or weak spines. In *constricta* this region of the style is provided with a small group of short black spines.

Hab. Victoria.

Holotype, ♂, Cann River, November 1928 (*J. Clark*).

Allotopotype, ♀.

Paratopotypes, several ♂ ♀.

Type in the National Museum, Victoria.

I take great pleasure in naming this species in honour of the collector, Mr. John Clark.

Limonia (*Geranomyia*) *bogongicola,* sp. n.

General coloration reddish yellow, heavily variegated with black; rostrum moderately elongate; femora brownish yellow, the tips broadly blackened; wings whitish to yellow, with a brown pattern; male hypopygium with the spines of the short rostral prolongation of the ventral dististyle of moderate length, but exceeding the prolongation itself.

Male.—Length (excluding rostrum) about 8–9 mm.; wing 8·5–10 mm.; rostrum about 3 mm.

Female.—Length (excluding rostrum) about 12–13 mm.; wing 10·5–11·5 mm.; rostrum about 4 mm.

Rostrum black, including the maxillary palpi, the latter 3-segmented; rostrum of moderate length only; subequal to the combined head in thorax in male, somewhat longer in the female. Antennæ black throughout, the basal segments weakly pruinose; flagellar segments cylindrical, the outer segments gradually increasing in length. Head black, pruinose.

Pronotum black, pruinose, restrictedly obscure reddish laterally. Mesonotal præscutum deep reddish, with three broad black stripes that restrict the interspaces; scutum brownish black; scutellum abruptly pale yellow, with a dark basal median spot; postnotal mediotergite dark brown, sparsely pruinose, the antero-lateral portions obscure yellow. Pleura chiefly black, sparsely pruinose, with vague indications of paler areas. Halteres yellow, the knobs weakly infumed, the stem fringed with setæ. Legs with the coxæ dark brown, more yellowish apically, the posterior coxæ more extensively so; trochanters obscure yellow; femora yellow basally, darker outwardly, the tips broadly blackened, in cases with a very indistinct pale apex; tibiæ brown, the tips blackened; tarsi black. Wings whitish subhyaline, more yellowish in female, with a restricted dark pattern, including the stigma, clouds at origin of *Rs*, Sc_2, along the cord and outer end of cell 1*st* M_2; additional paler washes in the medial, cubital, and anal cells. In the female the ground-colour is more yellowish and the pattern is heavier, including the broad apex and more distinct cloudings in the cubital and anal cells. Costal fringe relatively long and conspicuous in both sexes. Venation: Sc_1 ending opposite two-thirds to three-fourths the length of *Rs*, Sc_2 at its tip; *m–cu* close to the fork of *M*.

Abdominal tergites black, the caudal margins of the segments narrowly and indistinctly silvery; sternites more brownish, the caudal and lateral margins dark; hypopygium yellowish brown. Male hypopygium with the ninth tergite transverse, the caudal margin convex with the median area very gently emarginate. Ventral dististyle with the rostral prolongation short and stout, the two spines arising from tubercles that are placed close together, the spines longer than the entire prolongation. Ædeagus with the surface set with microscopic tubercles. Gonapophyses with the mesal apical lobe relatively prominent, the outer margin with microscopic denticles.

Hab. Victoria.

Holotype, ♂, Bogong High Plains, altitude 5600–6000 feet, January 1928 (*F. E. Wilson*).

Allotopotype, ♀.

Paratopotypes, 1 ♂, 1 ♀.

Type returned to Mr. Wilson.

The species is most closely allied to *L.* (*G.*) *risibilis* (Alexander), differing especially in the diagnostic features listed above.

Limonia (*Geranomyia*) *grampianicola*, sp. n.

Male.—Length (excluding rostrum) about 6·5 mm.; wing 7·5 mm.; rostrum about 2 mm.

Female.—Length (excluding rostrum) about 8 mm.; wing 8·5 mm.; rostrum about 2·4 mm.

Closely allied and generally similar to *L.* (*G.*) *risibilis* (Alexander), differing in the details of coloration and structure of the male hypopygium.

Rostrum of moderate length only, black, including the palpi. Antennæ black throughout. Head chiefly grey, the vertex with an extensive velvety-black area on either side of the median line, these areas narrower than the median region.

Mesonotal præscutum with three conspicuous black stripes, the median one broadest and most intense in front, the posterior portion and lateral stripes paler, the lateral areas crossing the suture on to the scutal lobes; median region of scutum and the scutellum extensively pale. Pleura chiefly yellow, the anepisternum and sternopleurite more infuscated, the dorso-pleural region dusky. All femora with black rings, most extensive on the fore femora, where they are nearly apical, there being only a restricted brightening beyond; on the other legs the pale femoral tups are subequal or a little shorter than the dark rings. Wings pale yellow, with a restricted brown pattern, including, besides the stigma, a small spot on Cu_1 near base, a rectangular area at origin of Rs, Sc_2, seams along cord and outer end of cell 1*st* M_2; a grey marginal wash in cell 1*st* *A*; veins black, *C*, *Sc*, *R*, *Cu*, and the prearcular veins pale. Venation: *Rs* strongly arcuated to angulated and short-spurred at origin; R_3 very long, approximately twice cell 1*st* M_2; cell 1*st* M_2 relatively short and broad, widened outwardly, at distal end about two-thirds as wide as long; *m–cu* variable in position, from one-fifth to approximately one-half its length before the fork of *M*.

Male hypopygium with the dorsal dististyle slender, the distal portion sinuous, the slender tip decurved. Rostral prolongation of ventral dististyle stout, the spines blackened, one arising from a low tubercle, the other more nearly sessile. Gonapophyses with the mesal apical lobe long and slender, their margins smooth. In *risibilis* the dorsal dististyle is differently formed, the rostral prolongation is stouter, and the spines are not blackened.

Hab. Victoria.

Holotype, ♂, Grampians, in fern-gully, October 1928 (*F. E. Wilson*).

Allotopotype, ♀.

Type returned to Mr. Wilson.

L. (*G.*) *annulata* (Skuse) has a somewhat similar leg-pattern, but a very different hypopygium.

Limonia (*Limonia*) *clarki*, sp. n.

General coloration dark grey, the pleura more or less distinctly striped; legs black, the femoral bases paler; wings with a strong brown suffusion, the oval stigma dark brown;

Sc relatively short, Sc_1 ending a short distance beyond the origin of *Rs*.

Male.—Length about 5–5·5 mm.; wing 6 mm.

Female.—Length about 7·5–8 mm.; wing 7–8 mm.

Rostrum elongate, nearly equal to the remainder of the head, black. Antennæ black throughout. Head grey, the posterior vertex infuscated on either side of the median line.

Pronotum and mesonotum dark brown, pruinose, especially laterally; præscutum with a broad median and narrower lateral brown stripes; median region of scutum, scutellum, and postnotum more heavily pruinose. Pleura grey, the dorso-pleural region darker brownish grey; dorsal portion of the sternopleurite paler. In some paratypes the pale pleural stripe is very evident. Halteres pale, the knobs dark brown. Legs with the coxæ brown; trochanters brownish yellow; femora pale basally, passing into black; tibiæ and tarsi black. Wings with a strong brown suffusion; stigma oval, dark brown; narrow vague dusky seams along cord, outer end of cell *1st* M_2, vein *Cu*, and the longitudinal veins beyond cord; veins dark brown. Venation: Sc_1 ending a short distance beyond the origin of *Rs*, Sc_2 at its tip; *Rs* relatively long, angulated near origin; *m–cu* at or close to the fork of *M*.

Abdominal tergites brownish black; sternites more pruinose, the basal sternites paler medially and on caudal margin; hypopygium chiefly dark, the ventral dististyle pale. Male hypopygium with the tergite transverse, the caudal margin gently emarginate. Basistyle with the ventro-mesal lobe low and stout. Ventral dististyle smaller than the basistyle, with a conspicuous cylindrical rostral prolongation that bears two long spines, one slightly more distal in position, a little shorter than the inner; both spines lie in an oval pale depression, the more basal spine from a short enlarged base. Dorsal dististyle a strongly chitinized black hook, the slightly decurved apex acute; margin of curvature of the style with small delicate setulæ. Gonapophyses broad-based, the mesal apical lobe slender.

Hab. West Australia.

Holotype, ♂, Mundaring, August 23, 1926 (*E. W. Ferguson*).

Allotype, ♀, Balingup, August 29, 1926 (*E. W. Ferguson*).

Paratopotypes, 7 ♂ ♀ (*E. W. Ferguson* and *J. Clark*); *paratypes*, 3 ♂ ♀, with the allotype (*E. W. Ferguson*); 4 ♂ ♀, Pemberton, August 28, 1926 (*E. W. Ferguson*); 1 ♂, Donnybrook, August 29, 1926 (*E. W. Ferguson*).

Type in the Macleay Collection.

Limonia clarki is respectfully dedicated to Mr. John Clark, in recognition of his valuable studies on the entomology of West Australia. The species is allied to *L.* (*L.*) *incisuralis* (Skuse) and *L.* (*L.*) *zonata* (Skuse), but is very distinct.

Limonia (*Limonia*) *tamborina*, sp. n.

General coloration yellow, the posterior præscutum and scutum dark brown; scutellum conspicuously whitish; pleura yellow, striped longitudinally with brown; knobs of halteres yellow; femora with a subterminal dark ring, the tips pale; wings cream-coloured, with a sparse dark pattern; *Sc* relatively short, Sc_1 ending shortly before mid-length of the angulated *Rs*; abdominal segments bicolorous, the bases obscure yellow, the apices more narrowly dark brown; male hypopygium with the mesal lobe of basistyle very long and slender, narrowed to an acute chitinized point.

Male.—Length about 5 mm.; wing 6 mm.

Rostrum and palpi black. Antennæ black throughout; flagellar segments oval, with a dense white pubescence and relatively inconspicuous setæ. Head dark brownish grey.

Mesonotum chiefly yellow, the præscutum behind with three confluent brownish stripes; scutal lobes dark brown; median area of scutum and the broad scutellum conspicuously whitish; postnotal mediotergite pale whitish yellow. Pleura yellow, with a broad dorso-longitudinal brown stripe that extends from the propleura, passing beneath the wing-root and across the pleurotergite to the abdomen; sternopleurite similarly darkened, producing a short ventral stripe. Halteres dusky, the knobs yellowish. Legs with the fore coxæ dark brown on outer face at base, forming part of the dorsal stripe; remaining coxæ and trochanters pale yellow; legs relatively long and slender, femora obscure yellow, darkened beyond base, gradually deepening to a narrow, dark brown, subterminal ring, the extreme tip again abruptly yellow; tibiæ obscure yellow, brightest at base, the tips darkened; tarsi brown. Wings with a creamy ground-colour, with a sparse dark pattern; stigma oval, brown; the brown clouds include conspicuous seams at Sc_2, origin of *Rs*, cord and outer end of cell 1*st* M_2; a broad diffuse seam in cell *M* adjoining vein Cu_1, becoming obsolete at mid-length of the cell; veins dark, more yellowish in the costal and prearcular regions. Costal fringe relatively short and inconspicuous. Venation: Sc_1 ends just before mid-length of *Rs*, Sc_2 longer, ending just beyond this point; *Rs* square at origin, weakly spurred ; R_2 and free tip of Sc_2 in transverse alignment ; inner end of cell R_3 lying far proximad of the other cells of cord ; cell 1*st* M_2 large, rectangular, as long as vein M_{1+2} beyond it ; *m–cu* shortly beyond the fork of *M*, subequal to the distal section of Cu_1.

Abdomen bicolorous, the bases of the segments obscure yellow, the tips more narrowly dark brown. Male hypopygium with the ventro-mesal lobe of the basistyle very long and slender, gradually narrowed to an acute chitinized point. Dististyle complex, trilobed ; what seems to correspond to the usual dorsal dististyle a short, nearly straight, pale rod, the apex narrowed and blackened ; main body of ventral dististyle a small fleshy lobe ; third branch corresponding to the rostral prolongation, this elongate, feebly chitinized, strongly curved at end, without rostral spines.

Hab. South Queensland.

Holotype, ♂, Mt. Tamborine, altitude 2000 feet, June 17, 1928 (*W. H. Davidson*).

Limonia (*Limonia*) *exosa*, sp. n.

General coloration of mesonotal præscutum yellow, with a brown median stripe ; posterior sclerites of mesonotum dark brown ; anterior vertex silvery ; antennæ relatively long, black ; wings with a distinct dusky tinge ; *Sc* long ; cell M_2 open by the atrophy of the basal section of M_3 ; *m–cu* at fork of *M* ; male hypopygium with the dorsal dististyle lacking ; ventral dististyle small, produced into a long arcuated chitinized blade.

Male.—Length about 3·6 mm. ; wing 4·5 mm.

Rostrum brownish yellow ; palpi brown. Antennæ dark brown throughout, of an unusual length for a member of this genus, if bent backward extending at least to the base of the abdomen ; flagellar segments long-oval, with a short, dark, glabrous, apical pedicel ; segments clothed with a dense white pubescence and short scattered verticils, the longest unilaterally arranged. Anterior vertex light silvery ; posterior portion of vertex dark brown, the posterior orbits light grey.

Pronotum brownish black. Mesonotal præscutum yellowish, with a broad brown median stripe that widens behind ; posterior sclerites of mesonotum dark brown. Pleura dark brown dorsally, the ventral portion paler. Halteres relatively long, dark brown, the base of the stem narrowly pale. Legs with the coxæ and trochanters yellowish testaceous ; femora light brown, the bases narrowly yellowish ; tibiæ pale brown; tarsi somewhat darker brown. Wings with a distinct dusky tinge, the oval stigma barely darker; veins brown, with relatively long, conspicuous, brown macrotrichia. Venation: Sc relatively long, Sc_1 extending to beyond mid-length of Rs, Sc_2 close to its tip; Rs weakly angulated at origin; free tip of Sc_2 and R_2 pale, the latter lying slightly more distad than the former; cell M_2 open by the atrophy of the basal section of M_3; *m–cu* at fork of M, a trifle shorter than the distal section of Cu_1; vein *2nd A* relatively elongate.

Abdomen dark brown, the eighth segment and hypopygium paler. Male hypopygium with the tergite strongly narrowed posteriorly, the caudal margin with a very low V-shaped notch. Ventro-mesal lobe of basistyle very large but low, applied to the whole mesal face of the style. Ventral distisyle small, oval, produced into a long arcuated chitinized blade. Dorsal dististyle lacking. Ædeagus very short and broad, the apex divided into two obtuse divergent lobes. Gonapophyses broad, the mesal apical angle produced into a long arcuated lobe that is gently widened outwardly, the tip obtuse.

Hab. New South Wales.

Holotype, ♂, Brooklana, Eastern Dorrigo, altitude 2000 feet, November 6, 1927 (*W. Heron*).

Paratopotypes, 6 ♂ ♂, February 1928 (*W. Heron*).

Limonia exosa is similar to *L. amicula* (Alexander) of North Queensland, differing in the diagnostic features given above.

Limonia (*Libnotes*) *tayloriana*, sp. n.

General coloration pale reddish yellow, the mesothorax unmarked with darker; head light grey; halteres and legs pale testaceous-yellow; wings subhyaline, the stigma subcircular, dark brown; veins pale, the cord and outer end of cell *1st* M_2 darker; male hypopygium with the spines of the rostral prolongation of the ventral dististyle very unequal in diameter.

Male.—Length about 5·5 mm.; wing 6 mm.

Rostrum moderately elongate, nearly as long as the remainder of head, pale brown; palpi obscure brownish yellow, 4-segmented. Antennæ dark brown; flagellar segments elongate-oval, each with a pair of outstanding verticils that are unilaterally arranged, these exceeding the segments in length. Head entirely light grey; eyes large, contiguous on vertex or virtually so.

Prothorax and mesothorax pale reddish yellow, entirely immaculate with darker; a whitish median line extends from the cephalic portion of the præscutum to the abdomen, widening out behind. Halteres short, pale. Legs pale testaceous-yellow, only the outer tarsal segments slightly darkened. Wings subhyaline, the base and costal region more yellowish; stigma small, nearly circular in outline, dark brown; veins pale yellow, the cord between the forks of *Rs* and *M* darkened; outer end of cell *1st* M_2 darkened; this dark coloration involves only the veins. Venation: *Sc* very long, Sc_1 extending to opposite *m–cu*; free tip of Sc_2 and R_2 in alignment; *Rs* about three times the basal section of R_{4+5}; cell *1st* M_2 elongate, the elements at outer end about in transverse alignment; *m–cu* at about two-fifths the length of cell *1st* M_2, subequal to the distal section of Cu_1; vein *2nd A* approaching *1st A* on the prearcular portion, thence gently sinuous and divergent.

Abdomen reddish yellow, the caudal margins of the segments narrowly and vaguely paler. Male hypopygium with the ninth tergite transversely rectangular, the caudal margin with a broad V-shaped notch, the lateral lobes with coarse conspicuous marginal setæ. Basistyle of moderate size, the mesal lobe low and obtuse. Ventral dististyle very large and fleshy, much larger than the basistyle; rostral prolongation relatively slender, with two spines that are very unequal in size, the outer spine placed just beyond mid-length of the prolongation, powerful and gently curved; inner spine near base of prolongation, very small and weak, setiform. Dorsal dististyle a curved chitinized rod, the apex acute. Ædeagus elongate, the apex with divergent flaps. Gonapophyses with the mesal apical angle long, slender, gently curved, the tip obtuse, the lateral margin with scattered pale spiculæ.

Hab. North Queensland.

Holotype, ♂, Mossman, March 1927 (*F. H. Taylor*).

Type in the Australian Institute of Tropical Medicine.

I take great pleasure in naming this species in honour of Mr. Frank H. Taylor, authority on the biting-flies of Australia. The fly is amply distinct from other regional species of *Libnotes*.

Limonia (*Dicranomyia*) *dicksoniæ*, sp. n.

General coloration brownish grey, the pleura clear blue-grey; antennæ black throughout; mesonotal præscutum with brown stripes, the median one more shiny black anteriorly; knobs of halteres infuscated; legs chiefly black;

wings grey, almost unmarked except for the stigma; *Rs* elongate, gently arcuate; male hypopygium with the tergite deeply emarginate medially.

Male.—Length about 6 mm.; wing 7 mm.

Female.—Length about 6·5 mm.; wing 8–8·2 mm.

Rostrum grey; palpi dark brown. Antennæ black throughout; basal flagellar segments subglobular, the outer segments passing to oval. Head light grey, the posterior vertex with a triangular dusky area on either side of a linear ashy median stripe; anterior vertex blue-grey, of moderate width.

Mesonotal præscutum dull yellowish grey, with three brown stripes, the median stripe more shiny black, especially in front; lateral stripes sometimes obsolete; posterior region of præscutum more brownish grey; scutal lobes brownish, the remainder of mesonotum clearer grey. Pleura clear blue-grey. Halteres of moderate length, pale, the knobs infuscated. Legs with the coxæ grey; trochanters brownish yellow; femora brown, the tips passing into dark brown or black; tibiæ and tarsi black. Wings relatively narrow, grey, the stigma oval, pale brown; scarcely indicated darkenings on other veins; cord and outer end of cell *1st* M_2 with extensive obliterative areas; veins dark brown. Venation: Sc_1 ending shortly before or beyond the origin of *Rs*, Sc_2 some distance before this tip; Sc_1 variable in length, from nearly as long as *m–cu* to considerably longer (♂); *Rs* long, gently arcuated, about twice the basal section of R_{4+5}; R_2 in approximate alignment with the free tip of Sc_2; *m–cu* shortly before the fork of *M*, usually from one-third to one-fourth its length.

Abdomen black, heavily pruinose, the hypopygium chiefly dark or obscure. Male hypopygium with the tergite large, the caudal margin deeply notched, the lateral lobes conspicuous, bordered with conspicuous setæ; a small transverse oval area on mid-length of tergite near caudal margin, this provided with two long and two more delicate setæ. Basistyle relatively large, the ventro-mesal lobe at its base, long and relatively narrow, provided with several stout flattened setæ in addition to smaller ones; at the base of this lobe a small tubercle set with about six long curved setæ. Ventral dististyle relatively small, fleshy, the rostral prolongation of moderate size, blackened, terminating in a small, chitinized, beak-like point; spines two, placed on the face of the prolongation at near mid-length, the inner spine a little longer and straighter than the slightly curved outer spine. Dorsal dististyle a gently curved rod that is narrowed at tip into a long spine. Ædeagus broad, trifid at apex. Ovipositor with the basal shields and valves fulvous-brown; tergal valves slender, gently upcurved, relatively small, but still much larger than in *whitei*.

Hab. Victoria.

Holotype, ♂, Ferntree Gully, April 15, 1928 (*F. E. Wilson*).

Allotopotype, ♀.

Paratype, ♀, Ringwood, May 5, 1928 (*F. E. Wilson*).

Type returned to Mr. Wilson.

Limonia dicksoniæ is generally similar to *L.* (*D.*) *whitei* (Alexander) of Victoria and Tasmania, but it is very distinct in the diagnostic features listed above. It likewise resembles *L.* (*D.*) *helmsi* (Skuse), but differs in the details of venation, as the long, gently arcuated *Rs*.

Limonia (*Dicranomyia*) *dorrigensis*, sp. n.

Belongs to the *liberta* (*tristis*) group; allied to *illingworthi*; size very small (wing, ♂, about 4 mm.); wings greyish, unmarked except for the stigma; male hypopygium with the gonapophyses very broad.

Male.—Length about 3·2 mm.; wing 4·1 mm.

Rostrum, palpi, and antennæ black; flagellar segments oval. Head dark grey.

Mesonotal præscutum yellowish grey, with three brown stripes; scutal lobes darkened; remainder of mesonotum more brownish grey. Pleura dark greyish brown. Halteres yellow, the knobs infuscated. Legs with the fore and middle coxæ extensively dark brown, the hind coxæ chiefly obscure yellow; trochanters reddish; remainder of legs brown, the tarsal segments passing into dark brown. Wings greyish, the oval stigma a little darker than the ground-colour; veins dark brown. Venation: Sc_1 ending about opposite the origin of *Rs*, the latter nearly three times the basal section of R_{4+5}; cell 1*st* M_2 elongate, longer than the veins issuing from it; *m–cu* more than one-half its length before the fork of *M*.

Abdominal tergites dark brown, the sternites more yellowish; hypopygium brownish yellow. Male hypopygium with the tergite transverse, the caudal margin evenly and convexly rounded, with a marginal series of setæ, including a median pair that are longer and stouter. Basistyle relatively small, the ventro-mesal lobe very stout, terminating in a dense brush of setæ; on face of style a small fingerlike lobe that is tufted with setæ that are considerably longer than the lobe itself; a small group of three or four strong setæ near the apical mesal portion of the basistyle. Dorsal dististyle a gently curved rod that is slightly expanded on outer half, thence gradually narrowed to a long apical spine. Ventral dististyle fleshy, including the broad rostral prolongation; the two rostral spines placed side by side, subequal in length, arising from low tubercles. Gonapophyses with the mesal apical lobe very broad, the outer margin weakly toothed, the lobe merging gradually with the main body of the apophysis.

Hab. New South Wales.

Holotype, ♂, Brooklana, Eastern Dorrigo, altitude about 2000 feet, February 10, 1929 (*W. Heron*).

Limonia dorrigensis is allied to *L.* (*D.*) *illingworthi* (Alexander), differing most evidently in the small size, wing-pattern, and structure of the male hypopygium, especially of the gonapophyses.

Limonia (*Dicranomyia*) *flavidella*, sp. n.

General coloration pale yellow; legs long and slender, the terminal tarsal segments darkened; wings pale yellow, the stigma vaguely darker; costal fringe relatively long and conspicuous; cell M_2 open by the atrophy of m.

Male.—Length about 5 mm.; wing 6 mm.

Rostrum and palpi pale yellow. Antennæ broken. Head ochreous-yellow.

Mesonotum and pleura uniformly reddish yellow, without markings. Halteres of moderate length only, pale yellow throughout. Legs long and slender, pale yellow, only the terminal tarsal segments infuscated; claws simple, except for a basal spine. Wings uniformly pale yellow, the stigma vaguely darker; veins darker yellow. Costal fringe relatively long and conspicuous. Venation: Sc short, Sc_1 ending opposite the origin of Rs, Sc_2 a short distance from its tip, Sc_1 alone about one-half the length of Rs; Rs about one-third to one-fourth longer than the basal section of R_{4+5}; cell M_2 open by the atrophy of m; m–cu at or shortly before the fork of M; distal section of Cu_1 a little shorter than m–cu.

Abdomen uniformly ochreous-yellow. Male hypopygium with the ninth tergite transverse, the caudal margin virtually straight across, each lateral angle with about a dozen setigerous punctures. Basistyle relatively short and stout, the ventro-mesal lobe large, conspicuously setiferous. Ventral dististyle large and fleshy, much larger than the basistyle, the rostral prolongation relatively slender, with two conspicuous spines; outer spine about three-fourths the length of the inner, placed a little more than one-half its length from the tip of the prolongation; spines placed close together. Dorsal dististyle a strongly curved hook, the long slender apex blackened. Gonapophyses very extensive, pale, the mesal apical angle curved to the obtuse tip. Ædeagus bifid at tip.

Hab. Victoria, New South Wales.

Holotype, ♂, Millgrove, Victoria, altitude about 1600–1700 feet, in a deeply shaded fern-gully, April 7, 1928 (*F. E. Wilson*).

Paratype, ♂, Eastern Dorrigo, New South Wales, altitude 2000–3000 feet, February 27, 1929 (*W. Heron*). "Beaten from tree-fern foliage, *Dicksonia antarctica*" (*F. E. Wilson*).

Type returned to Mr. Wilson.

Limonia (*Idioglochina*) *perkinsiana*, sp. n.

Allied to *tusitala*, Alexander; general coloration dark brownish grey; mesonotal præscutum brown, with four dark brown stripes; pleura dark brownish grey; legs dark brown, including the coxæ; wings with a strong dusky tinge; male hypopygium with the caudal margin of the ninth tergite bearing a small, deep, V-shaped median notch.

Male.—Length about 6 mm.; wing 7·5 mm.

Rostrum dark brown, nearly as long as the remainder of the head; palpi dark brown. Antennæ dark brown, the first segment more pruinose; flagellar segments strongly produced beneath, as in the *tusitala* group, the apical necks short and stout. Head pale reddish brown, sparsely pruinose, the median region of the vertex more infuscated.

Mesonotal præscutum with the interspaces brown, the disk with four dark brown stripes, the lateral and posterior portions of the sclerite dark greyish plumbeous; pseudosutural foveæ punctiform, dark brown; scutum light grey medially, each lobe with two dark brown areas; scutellum and postnotum light grey. Pleura dark brownish grey, the dorso-pleural membrane buffy. Halteres obscure yellow. Legs with the coxæ dark brown, pruinose, the apices restrictedly pale; remainder of legs dark brown, the femoral bases only a trifle brighter; claws with a series of about four teeth, the outermost longest. Wings with a strong dusky tinge, *Rs* and *Cu* more suffused with still darker brown; veins yellowish brown, some darker brown. Venation: *Sc* relatively long, the distance on costa between Sc_1 and origin of *Rs* about two-thirds the length of the latter; basal section of R_{4+5} about two-thirds *Rs*; R_{2+3} only gently arcuated; *m–cu* shortly beyond the fork of *M.*

Abdominal segments dark brown, the tergites vaguely more reddish brown medially at base; caudal margins of the segments very restrictedly pale; sternites obscure brownish yellow, darker laterally, the caudal margins narrowly pale; hypopygium more brightened. Male hypopygium with the caudal margin of the ninth tergite with a small but deep V-shaped median notch. Dorsal dististyle strongly curved, sickle-shaped, narrowed to the subacute apex. Ventral dististyle with the inner beak-like portion stout, the tip obtuse.

Hab. Queensland.

Holotype, ♂, Dunk Is., August 25, 1927 (*F. A. Perkins*).

I name this crane-fly in honour of the collector, Mr. F. A. Perkins.

Type in the University of Queensland.

Limonia perkinsiana is allied to *L.* (*I.*) *vilæ* (Edwards) and *L.* (*I.*) *novocaledonica*, Alexander, differing from both in the very dark colour and details of structure of the male hypopygium.

Eurhamphidia invenustipes, sp. n.

General coloration brownish grey; legs uniformly darkened; wings subhyaline, iridescent, the stigma and apex darkened.

Male.—Length about 6–6·3 mm.; wing 6·4–6·8 mm.

Rostrum approximately as long as the remainder of head, dark brown; palpi black. Antennæ short, brownish black, the first segment obscure yellow at base. Head brownish grey.

Pronotum dark brown. Mesonotal præscutum yellowish brown, with a narrow but conspicuous dark brown median stripe that does not extend to the suture; scutum pale brown, the centres of the lobes brownish black; scutellum and postnotum light brown. Pleura pale brown, pruinose, darkened dorsally; dorso-pleural membrane obscure buffy brown; sternopleurite darker brown. Halteres slender, dark brown, the base of the stem restrictedly obscure yellow. Legs long and slender; coxæ obscure yellow, the fore coxæ more infuscated; trochanters obscure yellow; femora brown; remainder of legs brown, without white markings. Wings highly iridescent, subhyaline; stigma elongate, dark brown; wing-apex narrowly darkened; veins dark brown. Venation: Sc_1 ending nearly opposite *r–m* or somewhat beyond it, Sc_2 not far from its tip; first section of *Rs* nearly twice the second; veins R_3 and R_{4+5} divergent apically; *m–cu* at near mid-length of cell 1*st* M_2, in approximate alignment with *r–m*.

Abdomen relatively long and slender, brownish black, the basal sternites obscure yellow.

Hab. West Australia.

Holotype, ♂, Donnybrook, August 29, 1926 (*E. W. Ferguson*).

Paratype, ♂, Pemberton, August 28, 1926 (*E. W. Ferguson*).

Type in the Macleay Collection.

Eurhamphidia invenustipes is entirely different from *E. niveitarsis* (Skuse), the only other described Australian species.

XI.—*Descriptions and Records of Bees.*—CXXII.

By T. D. A. Cockerell, University of Colorado.

Bombus discrepans, Pendlebury.

3 ♂, Koo Luang, Nakawn Sritamarat, Siam, April 30, 1928 (*Kerr*).

The genitalia, which differ considerably from those of any species known to me, were not described by Pendlebury. Spatha strap-shaped, parallel-sided, acutely pointed at apex; sagitta stout, very obliquely truncate apically, with the lower (outer) corner produced into a sort of short beak; stripes very broad at base, apically broadly truncate, for the attachment of the squama; squama black, somewhat U-shaped, with very thick base, outer arm broadly attached to stipes, but not projecting, inner much shorter, and pointed; volsella extending finger-like far beyond squama, the apex obtuse, somewhat broadened, its inner margin concave; stiff bristles project from beneath the apical portion.

The specimens were taken at an altitude of 1400 to 1600 m.

In its general appearance this bee is exactly like *B. ignitus*, Sm., from Japan.

Trigona ambusta, Cockerell.

Siam; Koh Po, Pattani, April 5; many from nest in hollow tree (*Kerr*).

The mesothorax and tegulæ are considerably darker than in the type. New to Siam.

Trigona bakeri, Cockerell.

Siam; Tung Nui, Satul, at flowers of *Melastoma malabaricum*, March 19 (*A. F. G. Kerr*).

The red spots at extreme base of antennæ are very obscure. New to Siam.

Trigona biroi, Friese.

Taken by Dr. Kerr at the same time, place, and flowers as *T. bakeri*. New to Siam; it is common in the Philippine Is. The abdomen is perfectly black.

Trigona atomella, Cockerell.

Siam; Chun Het, Trang (*Kerr*).

"Taken on my own hands, April 15."

Trigona heideri, Friese.

British Guiana; Amatuk, May 24 (*J. Ogilvie*).

Trigona longipes, Smith.

British Guiana; Amatuk, Kangaruma, and Tumatumari (*J. Ogilvie*).

Trigona clavipes (Fabricius).

British Guiana; Rockstone, June 2 (*A. Mackie*).

Melipona interrupta oblitescens, Cockerell.

British Guiana; Kaieteur, May 27 (*A. Mackie*).

Melipona fasciata barticensis, Cockerell.

British Guiana; Kaieteur, May 27 (*A. Mackie*).

Augochlora (*Pseudaugochloropsis*) *ogilviei*, sp. n.

♀.—Length about or nearly 7 mm., anterior wing 5·5 mm. Robust, very bright yellowish green, shining, the abdominal tergites very broadly margined with black; hair of head and thorax scanty, dull white, abundant on sides of face; scutellum with long black hairs, and an admixture of short black hairs on mesothorax; mandibles reddened apically; face broad; clypeus black except upper margin; supraclypeal area black; middle of face elevated, forming an obtuse ridge; front shining, with a strong median groove; ocelli rather large; flagellum dull rufous beneath except basally; angles of prothorax obtuse; mesothorax highly polished, appearing impunctate under a lens, but the microscope shows minute piliferous punctures; scutellum polished like mesothorax, and also the large area of metathorax, which has no radiating plicæ, but under the microscope shows an excessively fine transverse lineolation, tending toward reticulation; tegulæ dark reddish. Wings dusky, nervures and stigma dark brown; second cubital cell extremely high and narrow; first recurrent nervure meeting second intercubitus. Legs black, with pale hair, small joints of tarsi rufescent, anterior legs obscurely rufescent in front; hind spur with five long dark sharp spines. Underside of abdomen obscurely reddish.

Five from Rockstone, British Guiana, June 2 (*J. Ogilvie*, *A. Mackie*).

In Vachal's table this runs to *A. elachion* (Vachal), from Honduras, but differs at once in the sculpture and the non-metallic legs. It is a distinct and easily recognized species.

Augochlora phanerorhina, sp. n.

♂.—Length 7·5–8·5 mm., anterior wing 5 mm.

Very bright emerald-green, the hind part of thorax more yellowish green, hind margins of abdominal tergites very broadly black; hair of head and thorax extremely scanty, pure white on cheeks, but vertex, scutellum, and post-scutellum with dark plumose hairs; eyes deeply emarginate; face narrow, clypeal region strongly produced, forming a thick snout, the clypeus convex, polished, with very strong close punctures, the apical margin narrowly black; labrum and mandibles reddish; supraclypeal area densely punctured; front dull; flagellum short for a male, obscurely reddened beneath; mesothorax shining, strongly and closely punctured, at each side anteriorly dull from the density of the punctures; scutellum strongly punctured; angles of prothorax very prominent and sharp; area of metathorax shining, with strong radiating plicæ, but no well-defined polished margin, its width (antero-posteriorly) in middle a little less than that of the large postscutellum, the hind margins of both angulate; tegulæ very dark reddish brown. Wings dusky hyaline, the rather small stigma sepia, nervures dark brown; second cubital cell rather narrow, especially above; first recurrent nervure meeting second intercubitus. Legs largely black, with pale hair, but anterior femora behind, middle femora beneath, and hind coxæ bright green, anterior tibiæ ferruginous in front, tarsi more or less reddish. Abdomen shining, with sericeous white tomentum; venter black, not modified, except that the margin of the second sternite is obtusely angulate in middle.

British Guiana; type and one other from Amatuk, May 24 (*J. Ogilvie*); one from Waratuk, May 24 (*J. Ogilvie*).

Very near to *A. esox*, Vachal, but distinguished by the black margin of clypeus. Probably Vachal's *A. esox* was composite, and the specimen cited from British Guiana may have been this species. I will designate Cuzco, Peru, as the type-locality, as Peru was the only country from which Vachal had both sexes of the typical form. In Schrottky's table of "Oxystoglossæ" with hind margins of tergites black, our insect runs to the couplet including *A. iheringi*, Ckll., and *A. feronia*, Smith, but it is not very close to these.

Augochlora (*Augochloropsis*) *cataractæ*, sp. n.

♂.—Length nearly 10 mm., anterior wing 7 mm.

Bright emerald-green, the convex shining supraclypeal area blue-green, abruptly contrasting with the golden suffusion of sides of face; abdomen rather bluish green, with the depressed hind margin of second tergite (about twice as long as that of first) golden green; tegulæ large, entirely green; legs green as far as the basal part of basitarsi (more than half of hind basitarsi), beyond that black, the apical joint of front legs rufescent; hair of head and thorax tinged with fulvous, but white on cheeks and under side of thorax; an admixture of dark hairs on head and thorax above; head broad, orbits very strongly converging below; clypeus convex, very coarsely and densely rugoso-punctate, the apical margin very narrowly black; mandibles (which are simple) and labrum black; process of labrum very broadly and deeply emarginate; tongue dagger-like, not very long; antennæ black; angles of prothorax very broad, not prominent; mesothorax very densely and coarsely rugoso-punctate; scutellum also roughened, but anteriorly shining, in contrast with the adjacent mesothorax; area of metathorax smooth and shining, with very delicate weak radiating plicæ at sides; metathorax behind enclosure rough. Wings hyaline; stigma small, pale greyish brown; second cubital cell higher than broad; first recurrent nervure meeting second intercubitus, a little on the outer side. Abdomen shining, but finely rugulose, first two tergites regularly vibrissate, the bristles dark brown; tergites beyond the first with a thin clothing of black hairs; apex with at each side a tuft of very long reddish hairs; venter with the first three segments bright green with black margins, fourth brownish black with two green patches.

Kaieteur, British Guiana, May 27, 1929 (*Alice Mackie*).

The specific name recalls the falls, which have a height of 800 feet. In Vachal's table this runs near to *A. rudis* (Vachal), and must be closely allied, differing by the mainly green basitarsi and the measurements (wing 9 mm. in *A. rudis*). In Schrottky's Brazilian table it runs to *A. electra*, Sm., but that has yellow tarsi. It is somewhat allied to the differently coloured *A. heterochroa*, Ckll.

Augochlora (*Augochloropsis*) *semitoralis*, sp. n.

♀ (type).—Length about 6 mm., anterior wing 5·3 mm.

Robust, brilliant shining emerald-green, more or less golden at base of antennæ and along orbits, golden at extreme sides of base of area of metathorax and along hind margin of first tergite; or the inner orbital margins may be without golden, or the region near the base of antennæ may show coppery red; femora green, the hind femora very dark brown, not metallic, posteriorly; tarsi very dark brown, not at all metallic, except the hind basitarsi slightly at base in front; hair of head and thorax very scanty, pale, with an admixture of dark hairs dorsally; hind tarsi with copious pale ferruginous hair on inner side; vibrissæ (same in both sexes) weak and rather irregular, the bristles tinged with orange; head broad, orbits strongly converging below; apical middle (but not sides) of clypeus broadly black; labrum and the bidentate mandibles black; a brilliant green spot at base of mandibles; antennæ black; prothorax laterally rounded, not angulate; disc of mesothorax brilliantly shining, with well-separated punctures, but sides extremely densely punctured; scutellum shining, with well-separated punctures; area of metathorax with a narrow curved channel, regularly crossed by strong plicæ, the broad rounded margin highly polished; tegulæ green basally, dark red outwardly, the whole effect very dark. Wings hyaline, faintly dusky; stigma dilute greyish brown; nervures fuscous, the costal nervure dark brown; second cubital cell broad, not far from square; first recurrent nervure meeting second intercubitus or going slightly beyond. Abdomen broad, shining, the hind margins of tergites with a slight effect of thin hair-bands. Hind spur with seven extremely long slender black spines, tipped with reddish.

♂.—Similar, except for the usual sexual differences; clypeus prominent, with a broad dull white apical band; labrum and mandibles rufous, the extreme base of mandibles green; antennæ black, but the third joint somewhat swollen and red (compare the much larger *A. callichroa*, Ckll.); legs green, with knees, tibiæ obscurely at extreme apex, and the tarsi light ferruginous; venter of abdomen not modified, the first three sternites green.

5 ♀, Amatuk, British Guiana, May 24 (*J. Ogilvie*); 1 ♂, Kaieteur, May 26 (*A. Mackie*).

This little bee is very close to *A. toralis*, Vachal, but appears to differ, especially by the dark tegulæ and costal nervure of the female. Schrottky states that *A. toralis* is a synonym of *A. calypso*, Sm., and while our species is very close to *A. calypso*, it is certainly distinct by the orbits not edged with blue, the vibrissæ not conspicuous, and the wings not yellowish. *A. toralis* is said to range from Mexico to Bahia and Pará in Brazil, and it is very likely that the series is composite. Its spur is not described by Vachal. Perhaps the Brazilian specimens were *A. calypso*, and those from British Guiana *A. semitoralis*. It is greatly to be desired that someone having access to Vachal's collection in Paris should designate holotypes and type-localities, and inform us when the series contains a mixture of species.

Halictus potaroënsis, sp. n.

♀ (type).—Length fully 5 mm., anterior wing 4 mm.

Head and thorax nearly black, but with a perceptible metallic tint, the upper part of clypeus and sides of face dark green, supraclypeal area rosy red, cheeks green, vertex dark steel-blue, mesothorax and scutellum obscurely bluish, the scutellum slightly purplish, metathorax and pleura dark green; abdomen black, with the hind margins of the tergites rufescent; hair very scanty. Head rather oblong, with the clypeus prominent; mandibles dark, faintly reddened about the middle; clypeus shining, the apical portion black; inner orbits concave; front dull, very densely and minutely punctured (not striate); prothoracic angles prominent, rectangular; tubercles prominent, pointed; mesothorax shining, the surface microscopically tessellate, with scattered very minute punctures; scutellum moderately shining; area of metathorax large, the apical portion smooth and shining, the base minutely plicatulate; tegulæ very dark rufous, sparsely and weakly but evidently punctured (same in both sexes). Wings brownish hyaline, stigma large, very dilute brown, nervures fuscous, outer recurrent and intercubitus very weak; second cubital cell broader below than above, its lower side strongly oblique, receiving recurrent nervure a short distance before end. Legs black, with the tarsi and base of hind tibiæ dull ferruginous; hind spur with three long spines. Abdomen shining, thinly hairy, with a tendency to bands at sides of tergites 2 to 4.

♂.—Similar, except for the sexual characters; clypeus with a broad apical rufo-testaceous band; labrum red; mandibles mainly reddish; mesothorax shining dark green; hind knees, apex of their tibiæ, and the tarsi pale testaceous; antennæ only moderately long for a male, the flagellum pale testaceous or clay-colour beneath.

Kaieteur, British Guiana, May 27, 1929 (*Alice Mackie*).

Belongs to the subgenus *Chloralictus*, and is related to a series of Neotropical forms which are doubtless far more numerous than the present records show. *H. semiviridis*, Friese, from Bermuda, is smaller and less robust, with shorter face. *H. exiguiformis*, Ellis, from Guayaquil, has a much shorter and broader head and olive-green mesothorax. I do not find any species near enough to cause confusion.

Sphecodes biroi mariæ, subsp. n.

♂.—Length about 7 mm., anterior wing 6·3 mm.

General characters of *S. biroi*, Friese, with very broad face, covered with white hair, hairy eyes, no pubescent bands on flagellar joints, flagellum strongly nodose beneath; wings brownish, pale basally; first three abdominal tergites mainly red. Mandibles red in middle; flagellum entirely dark; tegulæ very dark, obscurely reddish externally; hind wings with eight hooks; first tergite with a broad hemispherical black patch, second blackened in middle, especially apically, third red only at base; tarsi brownish black, red only at apex.

Compared with the Philippine Is. *S. latifrons*, Ckll., it is seen to be very closely allied, but larger and more robust, with dark tegulæ, and base of metathorax more densely sculptured. The second and third tergites are more strongly and closely punctured than in *S. latifrons*. *S. abnormis*, Perkins, has testaceous tarsi and presents a number of other small differences. *S. dutti*, Blüthg., is also evidently different.

Siam ; Nan, Jan. 8, 1928 (*Cockerell*).

Named after Dr. Mary Collier, who collected many insects at Nan. The group of *S. biroi* cannot be fully elucidated at present. Blüthgen (1927) combines all the different forms (with a query in respect to *S. dutti*) under the specific name *S. biroi*, originally based on an insect from New Guinea. This seems to be going too far, though it is useful to call attention to the close alliance. I treat the Siamese insect as a subspecies, but suppose that eventually a series of closely allied species will be recognized.

Habropoda sutepensis, Cockerell.

Described from the male. The female, from the same locality (Doi Sutep, Siam), is similar, but larger and more robust, the dense hair of the abdomen very red. Clypeus convex, the upper third in middle with a shining keel, from the lower end of which starts a creamy-white vertical band, rapidly broadening below to form a broadly triangular pale area ; labrum reddish ; mandibles with more than the basal half pale rufous ; malar space well developed ; outer side of hind tibiæ with rich copper-red hair; hind basitarsi with black hair. The cheeks below have long pure white hair.

Osmia pseudamala, Cockerell.

Described from the male. Mr. R. Betensky has found both sexes at White Rocks, Boulder, Colorado, nesting in an old log. The female is somewhat over 10 mm. long, robust, steel-blue, with the front, vertex, occiput, mesothorax, and scutellum green ; mandibles tridentate ; hair of head and thorax above pale fulvous-tinted, mixed with black ; tegulæ half green. Legs black, hind femora green in front; ventral scopa black. In my table (Univ. of Colo. Studies, 1928) it runs nearest to *O. albolateralis*, Ckll., though the mesopleura has black hair on the upper posterior part, or may have it mostly black, in which case it runs to *O. malina*, Ckll. *O. albolateralis* has much longer and more conspicuous black hair on clypeus. *O. malina* is 9 mm. long, with hair of scutellum mainly black, and several other differences. Miss Sandhouse points out that the genitalia of *O. pseudamala* are highly distinctive, as she will describe in her revision.

XII.—*Three new Species of the Genus* Helotrephes* (*Hemiptera-Heteroptera*). By W. E. China.

The following descriptions are based on material sent for determination by Mr. G. L. R. Hancock, Assistant Government Entomologist in Uganda, and by Prof. H. B. Hungerford, of Kansas University, to whom I am indebted for the opportunity of examining the Helotrephid material discovered by him in the Amsterdam Museum.

In not a single case was a species of *Helotrephes* known from both sexes, and in only one case (*H. bouvieri* ♂) had it been possible to make dissections. Consequently the detailed structure of the female genitalia has hitherto remained unknown; so that it was extremely interesting to receive, through Prof. Hungerford, a series of specimens of both sexes. Owing, however, to paucity of material in the described species and to the absence of knowledge of the limits of variation, and considering the fact that each species probably exists in two structurally different forms (winged and wingless), it has been very difficult to decide on the identity of the Sumatran species. After much consideration and hesitation it has been decided to describe them both as new.

Helotrephes angulatus, sp. n. (Figs. 1 *a–g*; fig. 3 *d*.)

Colour (♀).—Dorsal surface pale sordid yellow marked with brownish black. Head brownish black, with an irregular-edged three-lobed border and some obscure markings on the disc and along base above the suture, pale sordid yellow (fig. 1 *a*); eyes and rostrum dark brown. Pronotum pale sordid yellow, the anterior margin along the suture brownish black, the posterior margin of this dark band strongly bisinuate, its lateral margins speckled, not reaching the lateral margins of the pronotum; posterior half of pronotum speckled with dark brown. Scutellum pale sordid yellow, moderately densely speckled with dark brown, with a large pale yellow spot at each side of base and a third in middle of base. Hemielytra pale sordid yellow, sparsely speckled with brown, the clavus and clavulus mottled with dark brown, a spot on corium at apex of clavus and the extreme apical margin of corium along interlocking device dark brown. Legs pale yellow, the coxæ, trochanters, bases of hind femora, and extreme apices of tibiæ and tarsi infuscate. Sternum and venter pale brown.

Structure (♀).—Seen in profile (fig. 1 *d*) the lateral margin of pronotum and lateral margin of head with a respective inclination of about 110°, the actual angle broadly rounded. Rostrum moderately long, extending just to the intermediate coxæ. First antennal segment (fig. 1 *c*) with its axis at right angles with the point of insertion, otherwise more or less cylindrical, with three or four scattered bristles on exposed surface, and a curious circular

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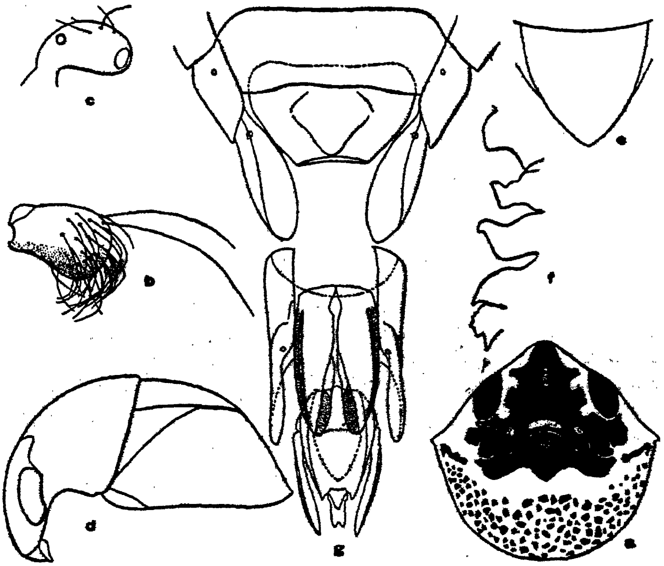
* For monograph of this genus, see 'Eos,' iv. pt. 2, pp. 129–172.

organ towards its base similar to that in *Idiocoris lithophilus*; second segment slightly longer than first, wider at apex than base, rounded apically, distinctly flattened, the outer surface covered with long, strongly-curved, flattened hairs, apex with two long filiform divergent bristles (fig. 1 *b*). Pronotum with the lateral margins distinctly carinate, the carina ending abruptly before the humeral angle to form an angulated tooth (fig. 3 *d*). Scutellum about as long as broad (fig. 1 *e*). Hemielytra with distinct claval suture, the clavulus well marked; costal margin of right-hand hemielytron devoid of a lateral lobe. Wings present, whitish hyaline, similar to those in *H. bouvieri*. Median prosternal keel strongly elevated, semihyaline, rounded anteriorly, acute-angled posteriorly, the posterior edge more or less perpendicular. Mesosternal carina strongly elevated, hyaline, wide at base, narrowed in middle, truncate at apex, which is produced anteriorly into a tooth. Metasternal carina broad, the anterior edge concave, the posterior edge short and straight, and the apex obliquely truncate, with anterior angle curved outwards and posteriorly (fig. 1 *f*). Front legs longer than the middle legs, the coxæ finely tuberculate and

Fig. 1.



Helotrephes angulatus, sp. n., ♀.

a, diagrammatic dorsal view of cephalonotum, to show colour-markings; *b*, second antennal segment; *c*, first antennal segment; *d*, profile view; *e*, scutellum; *f*, lateral view of median, sternal, and ventral carinæ; *g*, female genital segments.

covered on outer surface with long depressed hairs; femur thickest at base and tapering to apex, slightly longer than tibia (55:50), armed along inner side with longitudinal rows of short spines and longer bristles, the latter longer towards base; armed along outer side with a row of long semidepressed bristles, and a pair of long divergent bristles at base; tibia also armed along inner side with rows of short spines, bristles, and pectinate bristles; tarsus less than half the length of tibia (18:51), with inner rows of bristles and the usual apical structure; claws about one-third the length of tarsus. Middle legs similar to front legs but shorter, the femur distinctly longer than tibia (55:43), the bristles along its inner side longer towards base, those along outer side much shorter, the upper surface with a number of scattered short spines; tibial bristles longer, especially towards apex; tarsus nearly half the length of tibia, the claws about one-fourth the length of tarsus. Hind legs with femur shorter than tibia (59:72), inner side with two rows of short bristles, longest on basal half; tibiæ and tarsi with the usual long swimming-hairs and bristles; tarsal segments together nearly two-thirds the length of tibia, the second segment much shorter than first (19:25); claws about one-third the length of the first segment. Median keel of second abdominal sternite, seen in profile, strongly convex anteriorly and concave posteriorly, its apex acute and directed posteriorly, median keel of third abdominal sternite with a broad serrated basal lobe and a small posteriorly directed spur-like apical lobe (fig. 1 *f*); seventh sternite short, narrowed apically, the posterior margin concave, disc with a raised median triangular lobe; pleurites of seventh segment broad and concavely foliate; female genital segments (fig. 1 *g*) much narrower and more elongate than in *Tiphotrephes*, *Limnotrephes*, *Idiocoris*, or *Paskia*, otherwise similar in general plan, the eighth sternite split into two elongate lobes, with their inner apical extremities deflexed to form thickened flap-like appendices, pleural processes of eighth segment elongate, concave; ninth tergite with two elongate lobe-like lateral processes similar to the pleural processes of the seventh and eighth segments, and with a triangular anal flap representing the tenth segment (?); ninth sternite represented by a semitubular sclerite, the apex strongly emarginate, with the apical angles acute. An elongate style-like organ, with its apex bifid and with a small triangular lobe placed ventrally at its base, possibly represents the eleventh segment.

Total length 2·83 mm. Other measurements, see *H. hancocki*, sp. n.

Habitat.—Sumatra's O. K., Medan, 20 m.

Type, 1 ♀, 13. ix. 1921; paratypes, 1 ♀, 13. ix. 1921; 1 ♀, 3. x. 1921. J. B. Corporaal (Amsterdam Museum).

Allied to the Sumatran species *H. martini*, Kirk., which it resembles in general shape of the sternal and abdominal carinæ, shape of scutellum, and relative length of cephalonotum, but differs in the presence of the strongly-developed lateral pronotal carinæ with their angulate posterior extremities, absence of a lateral costal lobe on right-hand hemielytron of female, in the relative length of the hind tarsal segments, and in the presence of wings and a distinct claval suture.

The possibility of this species being the winged form of *H. martini* has been considered, but other details have been thought not sufficiently identical.

Helotrephes corporaali, sp. n. (Figs. 2 *a–g* ; figs. 3 *a–c*.)

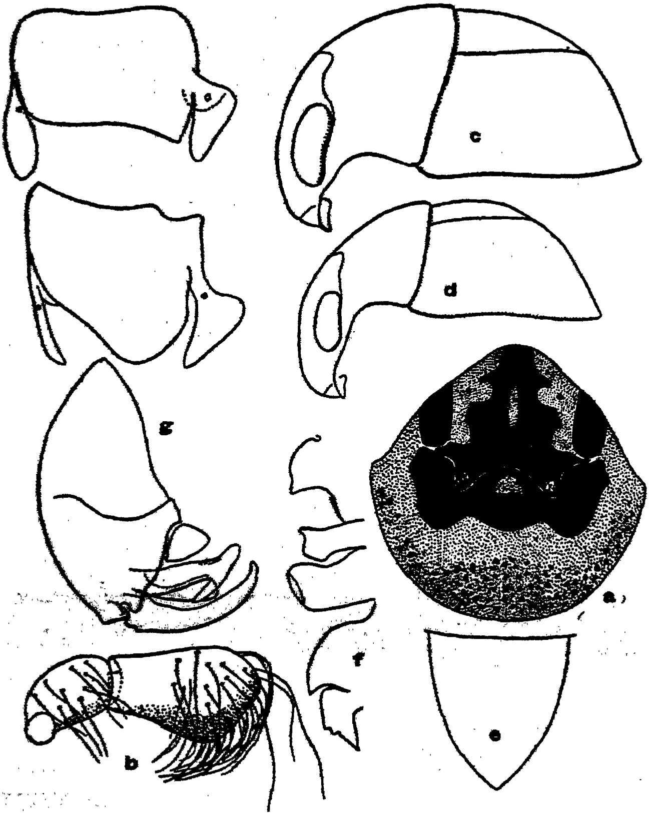
Colour (♂).—Dorsal surface greyish yellow marked with dark brown. Head dark brown, the anterior lateral areas in front of eyes, a large spot on middle of inner margin of eye, a small spot posteriorly on inner margin of eye, and an obscure narrow spot in middle of anterior disc fulvous-yellow; eyes and rostrum dark brown. Pronotum greyish yellow, the anterior margin along the suture dark brown, the posterior margin of this dark band bisinuate, its edges speckled and not reaching lateral margins of pronotum; posterior half of pronotum speckled with dark brown. Scutellum pale sordid yellow densely covered with the usual subchitinous brown speckling, and a dark brown band along basal margin which extends, less intensely, on to middle of disc in the form of a triangular mark. Hemielytra similar to scutellum, with a few indistinct brown marks over claval area and towards apex of scutellum brown. Legs fulvous-yellow, the coxæ, trochanters, base of hind femur, apices of front and middle tibiæ and tarsi moderately infuscate. Sternum and venter pale greyish brown.

♀.—Similar to ♂, but pale markings on head more or less confluent, forming a fulvous band along lateral margin of head and inner margin of eye, with its inner border irregular in outline; an obscure, almost obsolete, fulvous-brown longitudinal stripe extends down middle of disc; pronotum as in ♂, but with a light fulvous spot in middle of brown anterior band, just below the middle of the suture; scutellum without the triangular infuscation, but with a pair of transverse dark brown spots along posterior margin of anterior brown band.

Structure (♂ ♀).—Seen in profile (figs. 2 *c* & *d*), the lateral margin of pronotum and lateral margin of head with a respective inclination of about 130° (♂) or 110° (♀), the actual angle broadly rounded. Rostrum moderately long, extending to intermediate coxæ. Antenna (fig. 2 *b*) very similar to that in *H. bouvieri*, with the second segment trapezoidal but rather less broad at the apex and longer in proportion to its width (29:16). Pronotal lateral carina percurrent, not ending abruptly as in *H. angulatus* (fig. 3 *b*). Scutellum (fig. 2 *e*) slightly longer than broad at base (33:30 ♂, 40:37 ♀). Hemielytra without claval suture or clavulus, without a lateral costal lobe in ♀, wings absent or rudimentary. Median prosternal carina seen from side similar to that in *H. angulatus*, but with the posterior angle more acute. Mesosternal carina narrow, parallel-sided at base, slightly dilated towards apex, which is truncate, the anterior angle pointed, the posterior angle rounded. Metasternal carina broad, the anterior edge concave, the posterior edge straight, and the apex truncate; the apical extremity very thin in middle (fig. 2 *f*). Armature of legs similar to that in *H. angulatus*; relative measurements in ♂:—

	Femur.	Tibia.	Tarsus.	Claws.
Front leg	58	52	17	5
Middle leg	54	40	19	7
Hind leg	55	64	22 + 18	8

Fig. 2.



Helotrephes corporaali, sp. n.

a, diagrammatic dorsal view of cephalonotum ♀, to show colour-markings; *b*, antenna of ♂; *c*, profile view of ♀; *d*, profile view of ♂; *e*, scutellum; *f*, lateral view of median, sternal, and ventral carinæ of ♂; *g*, male genital segments.

Median keels of second and third abdominal sternites, seen in profile, similar to those in *H. bouvieri*, but that of the third more sinuate along its edge (fig. 2 *f*); seventh sternite in ♀ as in *H.*

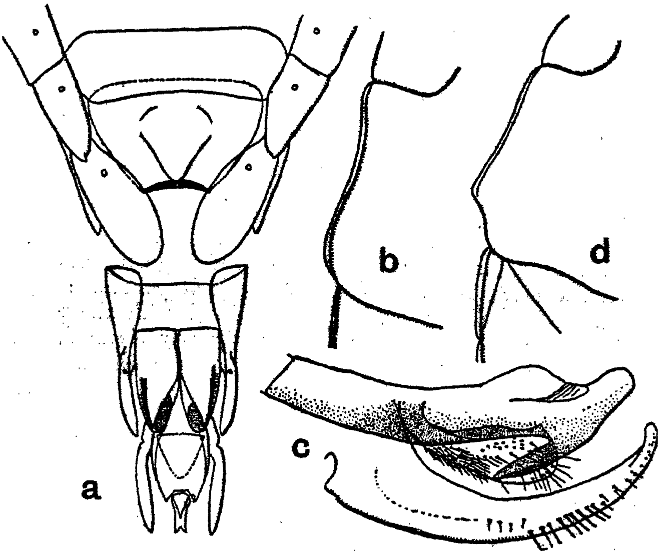
angulatus, the pleurites very broad and foliate. Genital segments in ♀ (fig. 3 *a*) very similar to those in *H. angulatus*, but the lobes of the eighth sternite much shorter. Genital segments in ♂ (fig. 2 *g*) very similar to those in *H. bouvieri*, but some slight differences in the shape of the pleurites; ventral paramere more curved at its apex, dorsal paramere more angular at its anterior apical angle, posteriorly directed barb of ædeagus relatively longer (fig. 3 *c*).

Total length, ♂ 2·67 mm., ♀ 3 mm. Other measurements, see *H. hancocki*, sp. n.

Habitat.—Sumatra's O. K., Medan, 20 m.

Type, 1 ♂, 3. x. 1921; paratypes, 2 ♂ ♂, 26. ix. 1921, and 2 ♂ ♂, 3. x. 1921, 1 ♀, 22. ix. 1921, 1 ♀, 26. ix. 1921, and 2 ♀ ♀, 3. x. 1921; also 2 larvæ, 13. ix. 1921.

Fig. 3.



Helotrephes corporaali, sp. n.—*a*, female genital segments; *b*, lateral margin of pronotum; *c*, male genitalia, showing hammer-headed ædeagus, long ventral paramere, and short dorsal paramere.

Helotrephes angulatus, sp. n.—*d*, lateral margin of pronotum, to show abbreviated carina.

Allied to *H. bouvieri* ♂ in the shape of antennæ, structure of ♂ genitalia, and in disproportionate lengths of hind tarsal segments. Differs, however, in much smaller size, shorter scutellum, and in the relative proportions of measurements CD & AD.

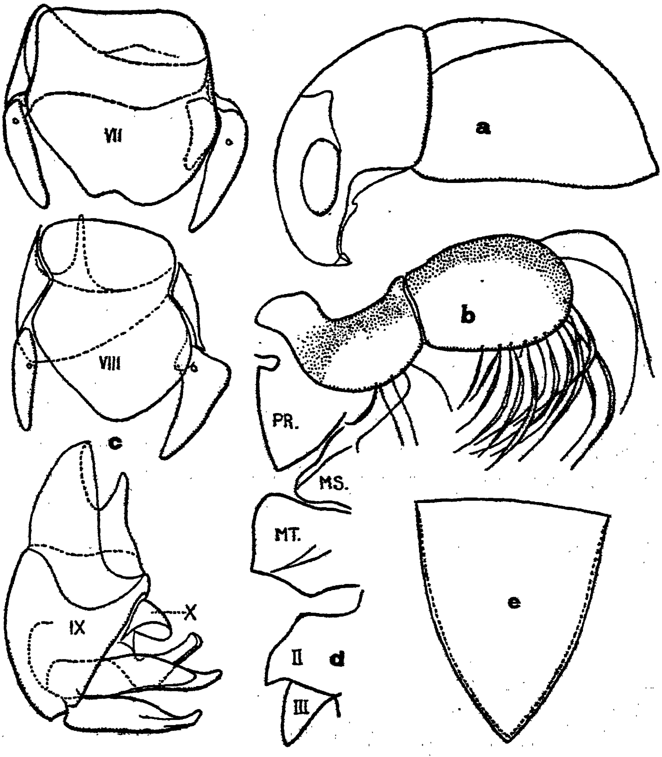
It is just possible that this species may be identical with *H. semiglobosus*, the length of which is given by Stål as 3 mm.

Helotrephes hancocki, sp. n. (Figs. 4 *a–e*.)

Colour (♂).—Very dark dull ferruginous-brown; eyes darker, almost black; a distinct border round eyes, a large obscure spot on each side of apex of head, a short longitudinal stripe on disc of cephalonotum just below centre of suture, posterior margin of pronotum, lateral pronotal plate, a small spot in middle of base of scutellum, a large spot on each side touching lateral margin near base of scutellum, a large obscure spot in corner of clavus between base of scutellum and posterior margin of pronotum, and a smaller spot in middle of base of corium very pale sordid yellow; scutellum paler towards extreme apex, which is obscurely pale sordid yellow; rostrum, apices of tarsi, and claws ferruginous-brown; legs brownish yellow, coxæ and basal third of hind femora dark brown.

Structure (♂).—Seen in profile (fig. 4 *a*) the lateral margin of pronotum and lateral margin of head with a respective inclination of about 110°. Rostrum moderately long, extending slightly beyond apices of anterior coxæ. Antenna (fig. 4 *b*) with the first segment curved almost at a right angle with its basal third, which is distinctly narrowed; apical half with a few long hairs; second segment longer than first, rounded and more broad apically, flattened dorso-ventrally, apical half covered with long, curved, flattened hairs, two long apical hairs less conspicuous than in *H. bouvieri* and *H. martini*; the segments in close contact, with apparently no stalk-like connection between them as in other species. Scutellum (fig. 4 *e*) much longer than broad at base (24 : 20), its apex angular. Hemielytra similar to those in *H. bouvieri*, regularly shallowly punctate, a short pale hair arising from each puncture; claval suture absent, the clavus and clavulus fused with the corium. Wings absent. Median prosternal keel strongly elevated, semi-hyaline in profile, more or less broadly lanceolate, directed posteriorly (fig. 4 *d*); mesosternal keel feebly elevated; metasternal keel strongly elevated, seen in profile very broad, anteriorly rounded, and posteriorly right-angled. Front legs longer than middle legs, the coxæ finely tuberculate and with long depressed hairs; femur thickest towards base, slightly longer than tibia, armed along inner side with longitudinal rows of short spines and longer bristles, and along outer side with a row of long semidepressed bristles, a hair at the base very long; tibiæ also armed along inner side with rows of spines, bristles, and pectinate bristles; tarsi about half the length of tibiæ, with inner rows of bristles, and with apical structure similar to that in *H. bouvieri*; claws about one-third the length of tarsus. Middle legs similar to front legs, but shorter, the femur distinctly longer than tibia (40 : 30), with the inner rows of spines and bristles becoming much longer towards base and with a number of scattered very short spines on upper surface; tibial spines longer, tarsus more than half the length of tibia (17 : 30), claws less than one-third length of tarsus; hind legs with the femur shorter than tibia (40 : 46), apical half of inside of femur with two rows of very short spines and no bristles, the femur suddenly constricted in the middle of the inner side; tibiæ and tarsi with the usual long swimming-hairs and bristles; tarsal segments equal in length, the claws about half the length of a single segment. Abdomen with the median basal keels of second and third sternites (fig. 4*c*) similar to those in *H. bouvieri*, but the left-hand pleural process of the seventh segment comparatively narrow, as in *Tiphotrephes*, not dilated and triangular, and the posterior margin of the seventh ventrite strongly posteriorly curved, with a concave apical sinuation, not truncate, as in *H. bouvieri*. Ventral paramere comparatively straight, broad, and parallel-sided for basal half, then more or less suddenly narrowed and ridged, the apex obliquely truncate. Dorsal paramere bent almost at a right angle in the middle, where it is very broad, but narrowed basally and apically, the apex shortly broadened and truncate. Ædeagus tubular, somewhat sinuate, gradually narrowed to a pointed apex, not hammer-headed as in *H. bouvieri* (fig. 4*c*).

Fig. 4.



Helotrephes hancocki, sp. n., ♂.
a, profile view; *b*, antenna; *c*, genital segments; *d*, median, sternal, and ventral carinæ; *e*, scutellum.

Total length 2 mm. Other measurements arranged as in "Monograph of Helotrephinæ" (for which see 'Eos,' iv. pt. 2, pp. 135–137).

	AB.	AD.	CD.	CE.	FK.	GH.	LM.	NO.	PQ.	T 1 : T 2.
H. angulatus ♀ ……	83	39	38	62	42	26	61	37	36	25 : 19
H. corporaali ♂ ……	77	37	35	54	36	23	51	33	30	22 : 17
H. corporaali ♀ ……	87	37	39	65	44	27	64	40	37	26 : 20
H. hancocki ♂ ………	57	24	24	40	30	19	39	24	20	16 : 16
H. hancocki ♂ ………	60	26	27	40	30	19	39	24	20	16 : 16

Habitat.—Uganda, Kampala, Lake Victoria.

Type, ♂; paratypes, 2 ♂; and 1 larva, 30. vi. 1929 (*G. L. R. Hancock*).

Distinguished at once from all other species of *Helotrephes* by small size. Allied to *H. hungerfordi* from French Equatorial Africa, but much smaller, without a claval suture, and with the prosternal carina with its posterior angle acute. There is a remote possibility that this species may eventually prove to be the wingless male of *H. hungerfordi*. The structure of the ædeagus in *H. hancocki* is apparently not typical of that in *Helotrephes*, but until males of more species of the genus are known it is impossible to decide if this character is of subgeneric importance.

The structure of the female genitalia in the Helotrephinæ, while similar in general plan to that in the Idiocorinæ, differs in the more elongate form and in the presence of a semitubular apical abdominal segment, which may represent either the tenth or eleventh segment.

PROCEEDINGS OF LEARNED SOCIETIES.

GEOLOGICAL SOCIETY.

October 23rd, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

The following communication was read:—

'The *Petalocrinus* Limestone Horizon at Woolhope (Herefordshire).' By Roy Woodhouse Pocock, M.Sc., F.G.S.

Upper Llandovery sandstones surmounted by Woolhope Limestone beds form the core of the Silurian anticline of Woolhope. These two groups are separated by a thickness of some 20 feet of Transition Shales with thin bands of limestone. One of these limestone-bands, averaging an inch in thickness, occurs in the Transition Beds about 5 feet from their summit, and is composed mainly of the remains of the crinoid *Petalocrinus*, which has been recorded from Sweden and North America, but has not hitherto been found in Britain.

The most striking peculiarity of the crinoid is the fusion of the arms into five solid arm-fans or petals, which radiate from the dorsal cup. The arm-fans are usually found detached in the limestone, throughout which they are profusely scattered.

A bed of large tabulate corals on which the *Petalocrinus* Band rests is found in this association throughout the outcrop. The combined thickness of the crinoid and coral-beds varies between 3 and 6 inches.

Llandovery rather than Wenlock affinities are indicated by the fauna of the Transition Beds.

Detailed mapping of the outcrop of the limestone-band has revealed interesting and unexpected features in the structure of the area, which appears to have been subjected to pressure, mainly along a north-west and south-east axis, developing thrust-faulting approximately at right angles to that axis.

Evidence is advanced in favour of a late Coal-Measure age for the principal movements that gave rise to the anticline.

At May Hill and at Malvern the *Petalocrinus* Limestone, with its associated coral-bed, has been detected at the same horizon as at Woolhope.

November 6th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

The following communication was read:—

'Fossil Insects of the South Wales Coalfield.' By Herbert Bolton, D.Sc., F.R.S.E., F.G.S.

The Author describes a collection of fossil wings from the South Wales Coal Measures numbering nineteen specimens. Several are too fragmentary for determination of genus or species, or both; the remainder are referable to the Palæodictyoptera and Blattoidea.

To the first order two new species are ascribed, and to the latter ten species, the remainder being Blattoid wing-fragments too incomplete for determination.

The Palæodictyopteron wings are referred to the genus *Lithosialis*, hitherto only known from the Coal Measures of Coalbrookdale (Shropshire).

The Blattoid species are referable to the family Archimylacridæ, three species; and the tribe Hemimylacridia, seven species. The stratigraphical range of insect-remains is from the Triquart Seam of Tumble (South Wales) of Westphalian age, through the Staffordian upwards to the Penyscallen Seam of Gorseinon (Glamorgan) in the Radstockian.

Palæontologically, the insect-fauna of South Wales now shows relationships with the insect-faunas of the Midland and Northern coalfields, and a close approximation to forms already known from the Coal Measures of Coalbrookdale (Shropshire), the Forest of Dean, and those of Kent, while several of the Hemimylacridian forms are identical with species described by Prof. Pierre Pruvost from the Coal Measures of Pas-de-Calais (Northern France).

The South Wales Coal Measure insect-fauna thus approaches more nearly to the Pas-de-Calais facies than to that of any British coalfield.

The occurrence of two species of *Lithosialis* in the South Wales coalfield links up these measures with those of the Midlands and the North of England, from which twelve families and seventeen genera are known. An intermediate link is supplied by *Lithosialis brongniarti* Mantell from the Coal Measures of Coalbrookdale (Shropshire), while *Lithomantis carbonarius* Woodward, from the Scottish Coal Measures, is a near ally.

The Welsh forms of Palæodictyoptera do not give much assistance in faunal or stratigraphical relation.

The Welsh Blattoids, however, are now sufficiently numerous and varied in character to justify comparison with the more abundant suite of forms recorded from the Coal Measures of Staffordshire and the Pas-de-Calais.

Certain species are common to both areas. *Archimylacris atrebatica* Pruvost, from the Big Vein, Cross Hands, is also found in the Assise d'Anziers, both horizons being Westphalian.

The genus *Phyloblatta* in both areas ranges from the Westphalian upwards into the Radstockian. An *Archimylacris pronotum*, from the Gwernau Level near Maes-y-Cwmmer (South Wales), is more nearly akin to the typical French species *pronotum* of this genus, figured by Prof. Pruvost, than to any British form.

It is, however, when we compare the South Wales examples of Hemimylacridia with the French species that we find the closest relation.

Hemimylacris is represented by two species from seams in the Radstockian of South Wales, comparable with two of Pruvost's species from the Faisceau d'Edouard, Assise de Bruay, which is also Radstockian. *Phylomylacris*, of which ten species are recorded in the Faisceau d'Edouard, is represented by one species from the Loughor vein; by two (possibly three) from the Penyscallen Seam of Beili Glas Colliery, Gorseinon, both in the Radstockian; and by a doubtful species in the No. 2 Rhondda Seam of the Staffordian. With the exception of this last doubtful species, *Phylomylacris* is restricted to the Radstockian in both the Welsh and the Pas-de-Calais areas. The genus *Soomylacris* presents even stronger evidence. Two new species, recorded in the paper, are from the Swansea 5-foot Seam, and the Mynyddislwyn Vein of the Radstockian. Two species are known from the Forest of Dean, extending the range of the genus to the north-east, and one species has been recorded from the Barfreston boring in the Kent Coalfield, which provides evidence of unity with the two species that Prof. Pruvost has recognized from the Insect-Bed of Liévin in the Pas-de-Calais. Thus it may be said that the three typical Hemimylacridian genera found in the South Wales coalfield are present also in the coalfields of Lens and Liévin.

Prof. Pruvost, in his 'Distribution des Faunes Insectes Paléozoiques' p. 318, indicates that the upper beds of the British Staffordian are equivalents of beds of Faisceau d'Ernestine age in the Assise de Bruay.

It seems evident from the distribution of the Welsh insect-wings that this generalization holds good in the Welsh area, for, correlated by the insect-fauna alone, the whole of the Radstockian of South Wales, and a portion of the Upper Staffordian down to the Swansea 2-foot Seam, should be regarded as the equivalent of the Assise de Bruay.

These conclusions also tend to confirm the view of Dr. A. E. Trueman, who, after an exhaustive study of the molluscan zones of the South Wales coalfield and those of the Faisceaux of the Pas-de-Calais Coal Measures, expressed the opinion that the two areas were so similar as to provide a basis for correlation.

Prof. A. H. Cox's suggested correlation of the Coal Measures of South Wales with those of Staffordshire upon lithological grounds seems likely to be supported by the insect-fauna, for, outside the Welsh area, the genera *Archimylacris* and *Aphthoroblattina* are known only from the Shropshire and Staffordshire coalfields.

November 20th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

The following communication was read:—

'The Geology of the Country between Nant Peris and Nant Ffrancon (Snowdonia).' By David Williams, Ph.D., M.Sc., B.Eng., D.I.C., F.G.S.

The area described lies immediately north of Snowdon, between the Passes of Llanberis and Nant Ffrancon. The general stratigraphical succession is as follows:—

				Thickness in feet.
TERTIARY.		Olivine-Dolerite Dykes.		
LOWER CARADOC to MIDDLE LLANDEILO.	Snowdon Volcanic Suite.	Bedded Pyroclastic Series.	Pumice-tuffs... Upper limit not seen.	
			Andesitic basalt	200
			Banded pumice-tuffs	500
		Lower Rhyolitic Series.	Flinty rhyolite-tuffs	250
			Slates, with tuff-bands	250
			Vitric tuffs, with thin flows	500
			Grits and slates, with tuff-bands	200
			Nodular rhyolites	Up to 50
			Massive and banded rhyolites	200
LOWER LLANDEILO and LLANVIRN.		Gwastadnant Grits, with rhyolites and keratophyre		750
		Talgau lavas (soda-rhyolite and keratophyre)		300
		Dark slates (from about the *Nemagraptus-gracilis* Zone to below the *Didymograptus-murchisoni* Zone)		2000+

		Thickness in feet.
TERTIARY.	Olivine-Dolerite Dykes.	
	—— Arenig Beds unexposed. ——	
CAMBRIAN—		
UPPER.	Ffestiniog Grits	1000
	Maentwrog Slates	1000
	Bronllwyd Grits	Up to 1500
MIDDLE.	Green Slates at the top of the Cambrian 'Slate-Belt'	100
EARLY INTRUSIVES.	Bwlch-y-Cywion 'granite' and Moel Perfedd Granophyre (? Llandeilo age).	
	Dolerite-sills and dykes of pre-cleavage age (? Upper Llandeilo or Caradoc).	

The topmost Cambrian beds, the Ffestiniog or *Lingula* Grits, are of shallow-water origin. Near their base they have yielded *Olenus micrurus*, whereas their topmost 150 feet carry abundant *Lingulella davisii*, and may be equivalent to the *Lingulella* Band of the Portmadoc country. They are faulted against blue-black slates, probably of Lower Llanvirn age. The lowermost graptolites thus far recovered from these slates are referable to the lower part of the zone of *Didymograptus murchisoni*. Upwards, the slates pass into the paler Llandeilo slates with *Glyptograptus teretiusculus*, at the top of which occur the Talgau lavas apparently belonging to the Glyder Fach–Capel Curig volcanic suite. By contrast with the overlying Snowdonian lavas, from which they are separated by the Gwastadnant Grits, these earliest flows are notably sodic.

The Snowdon Volcanic Suite is essentially composed of potash-rhyolites and rhyolite-tuffs, succeeded, near the Devil's Kitchen, by pumice-tuffs and flows of andesitic or basaltic character. The Upper Rhyolitic Series of Snowdon itself is here absent.

Two large acid plutonic masses, Moel Perfedd and Bwlch-y-Cywion, are believed to represent the denuded plugs of the vents from which the Lower Rhyolitic Series was extruded. Differentiation within the Bwlch-y-Cywion 'granite' is discussed, and some results of contact-metamorphism are described.

A number of pre-cleavage sills and dykes of augite-dolerite and spilitic dolerite are intruded among the Llandeilo beds, and some highly decomposed quartz-dolerites are injected into the Llanvirn Slates.

Both the folding and the cleavage, which strike approximately north-east and south-west, are attributed to Caledonian earth-movements, the cleavage following closely upon the folding, but preceding the faulting. 'Cleavage-fans' are conspicuous, two 'synclines' being separated by an 'anticline'. There appears to be no evidence in this area of the post-cleavage thrusting observable on Snowdon.

THE ANNALS

AND

MAGAZINE OF NATURAL HISTORY.

[TENTH SERIES.]

No. 26. FEBRUARY 1930.

XIII.—*Descriptions of the Type-specimens of some Carboniferous Corals of the Genera* "Diphyphyllum," "Stylastræa," Aulophyllum, *and* Chætetes. By Stanley Smith, M.A., D.Sc., F.G.S., and W. D. Lang, M.A., Sc.D., F.R.S., F.G.S.

[Plates VII. & VIII.]

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INTRODUCTION.

Fleming's material is in the Royal Scottish Museum, Edinburgh, and the corals were kindly lent to us by

Dr. J. Ritchie. Most of these were of historical interest only, adding nothing to our knowledge of the species founded by Fleming in his 'History of British Animals'; yet they include the four holotypes, which are here described.

Whilst revising Fleming's types, we have taken the opportunity to describe also certain others, namely, those of the species *Diphyphyllum lateseptatum* and *D. gracile,* which belong to the same genus as Fleming's *Caryophyllea fasciculata*; *Stylastræa inconferta* and *S. basaltiformis,* which bear the same relation to the cerioid *Lithostrotion* as *Diphyphyllum* does to the phaceloid forms of that genus; and *Chætetes radians,* which is conspecific with Fleming's *Favosites septosus.* We also discuss all the genera involved.

We thank Dr. J. Ritchie for the use of the Fleming specimens, and Prof. J. E. Marr for permitting one of us (S. S.) to cut M'Coy's types, which are in the Sedgwick Museum, Cambridge. Such of Lonsdale's specimens as are mentioned are in the British Museum, if not lost.

LITHOSTROTION, Fleming, 1828, p. 508.

Genotype: *L. striatum,* Fleming, 1828, p. 508=*Lithostrotion sive Basaltes minimus striatus et stellatus,* Edward Lhwyd, 1699, p. 124, pl. [xvi.]*; 1760, p. 125, pl. xxiii.

Diagnosis.—Phaceloid and cerioid Rugose Corals, which have, typically, a columella, long major septa, and large tent-shaped tabulæ, usually supplemented at the theca by smaller and nearly horizontal tabulæ. Dissepiments are well developed in the larger species, but absent in the very small forms. Gemmation is non-parricidal. Diphymorphs of *Lithostrotion* have no columella, short septa, flat or distally arched tabulæ, and, in the phaceloid forms, parricidal gemmation.

Lithostrotion=*Stylastræa,* Lonsdale, 1845, p. 619.

Non *Stylastræa,* de Fromentel, 1861, p. 223.

Genotype of *Stylastræa*: *Lithostrotion sive Basaltes minimus striatus et stellatus,* Lhwyd, 1699, p. 124. This is the genotype of *Lithostrotion,* see Smith, 1916, p. 220, therefore *Stylastræa* is an absolute synonym of *Lithostrotion.*

Lonsdale expressly founded *Stylastræa* upon Lhwyd's Coral, but under two misapprehensions: first, that *Lithostrotion etc.,* Lhwyd, had no persistent columella; and, secondly, that *Lithostrotion striatum,* Fleming, was generically identical with Fleming's *L. floriforme* (Martin's "*Erismatolithus Madreporites* (*floriformis*)"). Even if Lhwyd's coral has some ambiguous features, it certainly has a columella, and Fleming explicitly founded his *Lithostrotion striatum* upon it. What we do not completely know are certain structural details and the exact size of the corallites. *Madrepora vorticalis*, Parkinson (1808, p. 45, pl. v. figs. 3 & 6) and *Astrea basaltiformis*, Conybeare & Phillips (1822, p. 359), were also founded upon Lhwyd's description and figure. Martin's coral is quite different and is well known.

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* See S. Smith, 1916, p. 220. The matter of the genotype of *Lithostrotion* is at present before the International Committee of Zoological Nomenclature, and we intend to discuss it further in a later paper.

It is interesting to note that non-columellate (diphymorph) corallites are much rarer among cerioid colonies of *Lithostrotion* than they are among the phaceloid forms. Both Lonsdale and M'Coy, however, have described examples of cerioid non-columellate *Lithostrotion* as *Stylastræa conferta* and *S. basaltiforme*, respectively. These differ from the phaceloid non-columellate *Diphyphyllum* in their marginal, non-parricidal gemmation; in their tabulæ, which are not differentiated into a distinct inner and outer series; and in their coarser dissepiments. We have seen that *Stylastræa* is an absolute synonym of *Lithostrotion*; and, therefore, propose the name {*Diphystrotion*} for these diphymorphs of cerioid *Lithostrotion*. It will be noted that {*Diphyphyllum*} and {*Diphystrotion*}, though differing from *Lithostrotion* in what might reasonably be supposed to be generic characters, yet do not constitute true genera, but are expressions of a trend which some external or internal stimulus has provoked to rapid development in a colony, or in certain individuals of a colony, so that the individual anticipates an evolution which is familiar in other stocks, both nearly and distantly related, and is there seen to be a phyletic, and not an individual, trend—a trend which results in new generic forms. We propose to call these forms which anticipate, but do not constitute, new genera—*genomorphs*; and to indicate them by genomorphic names, which are to be recognized as such by being placed in braces.

Moreover, in order to avoid confusion, the diphymorph trivial name might also be retained after the genomorphic name. Thus, "*Lithostrotion* sp. {*Diphyphyllum lateseptatum*} probably = *Lithostrotion* {*Diphyphyllum*} *martini*" would mean that what was formerly considered to be the species *Diphyphyllum lateseptatum* is but a diphymorph form of *Lithostrotion*, probably of *L. martini*. By this means a new concept has been expressed by adding genomorphic names to Linnæan nomenclature.

Lithostrotion, Fleming, 1828, p. 508, genomorph {*Diphyphyllum*, Lonsdale}.

Genomorphotype: *Diphyphyllum concinnum*, Lonsdale, 1845, p. 624, pl. A. fig. 4 (the genotype of the original genus *Diphyphyllum*). The type of *D. concinnum* is lost; we therefore base *Diphyphyllum* on *D. lateseptatum*, which, if not conspecific, is certainly congeneric with *D. concinnum*.

Diagnosis.—Phaceloid *Lithostrotion*, which have no columella, or one which is reduced to spines on successive tabulæ. The axial tabulæ may be flat or convex, but have downturned edges, which either meet the tabulæ below them or extend to the dissepimental wall; the outer smaller tabulæ abut against the inner tabulæ. The dissepiments, which are small, are well developed in the larger forms. Gemmation is parricidal.

Remarks.—*Diphyphyllum* is generally used not only for phaceloid forms of *Lithostrotion*, but for any phaceloid coral with short septa. Such corals in some instances have followed the same trend as the "diphymorphs" of *Lithostrotion*—a trend almost universal in Rugose lineages, in which the septa retreat from the axis; in other instances their short septa may constitute a primitive character. We would restrict the genomorphic name {*Diphyphyllum*} to the diphymorphs of *Lithostrotion*, considering, as we have already suggested, that in this group the diphymorph structure is a condition due to other causes than normal phyletic development; and that a suitable stimulus may start any individual along this trend. Diphymorph variants accompany columellate *Lithostrotion* throughout the known range of the genus; but they first appear at a horizon slightly lower than that at which the lowest columellate *Lithostrotion* has yet been found. In these early diphymorphs the axial tabulæ are almost horizontal and inosculate with the small outer tabulæ (*Diphyphyllum* α of S. Smith *). It is probable, therefore, that they represent a primitive stage of *Lithostrotion*, while the characteristically later diphymorphs (*Diphyphyllum* β of S. Smith *) with strongly arched inner tabulæ show a reversionary trend. This point, however, needs to be established by further investigation.

Lithostrotion sp. {*Diphyphyllum concinnum* (Lonsdale)}.

Diphyphyllum concinnum, Lonsdale, 1845, p. 624.

Carboniferous Limestone. Hill of Tchirief, Kamensk, on the River Issetz, eastern side of the Ural Chain.

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* 1928, p. 114.

The syntypes of {*Diphyphyllum concinnum*} cannot be traced, but they consisted, according to Lonsdale (*loc. cit.*), of "one subdivided stem (figs. 4 *a*, 4 *b*) and several portions of others (fig. 4); the larger having a nearly uniform diameter of four and a half lines [9 mm.], and the smaller of three and a half lines." Lonsdale's description and figures clearly indicate a form which closely approaches M'Coy's {*Diphyphyllum lateseptatum*}, both in details of structure (*q. v.*) and in size, but slightly larger, and with the dissepimental area relatively wider. From Lonsdale's statement it would appear that the axial tabulæ in {*D. concinnum*} occupied only half the diameter of the corallite, whereas in {*D. lateseptatum*} they occupy two-thirds. There are over 30 major septa. Since the type-specimens are no longer available, Lonsdale's description may be quoted here in full: "Stems cylindrical, nearly smooth; crossed externally by close, fine, waved lines, and stronger, unequal, distant bands; lamellæ numerous, variable; inner surface of plates furrowed strongly upwards and outwards; central area, diaphragms flat, convex or irregular; intermediate area, principal lamellæ exceeding 30, more or less waved, intermediate very unequal; interstitial prolongations of diaphragms inclined sharply downwards, accessory plates nearly horizontal; outer area, lamellæ variable in strength and range, interstitial plates largely vesicular; terminal cup deep, lined by edges of the lamellæ, no central boss."

The statement in the original description that the inner surface of the plates (septa) are furrowed rather suggests that the undulations which characterise the sides of the septa of the holotype of *Stylastræa inconferta* are also present in this coral. Until topotype material is available, this form cannot be certainly identified nor the name authoritatively used.

Lithostrotion sp. {*Diphyphyllum lateseptatum* (M'Coy)}. (Pl. VII. figs. 1–4.)

Diphyphyllum lateseptatum, M'Coy, 1849, p. 8; 1851, p. 88, pl. iii. *c.* figs. 10, 10 *a*, *b*.

Holotype.—Sedgwick Museum, Cambridge. Specimen No. 123, Carboniferous Limestone, Corwen.

The specimen is a piece of dark-coloured limestone, 4·5 cm. × 3·5 cm. × 0·3 cm. It has been broken, but the pieces fit together. It enclosed fourteen fairly straight, more or less complete, corallites, which stand out from its upper weathered surface, and are well exposed as longitudinal sections on one of its sides. The type-material also includes an isolated and broken corallite, figured by M'Coy (fig. 10 *a*), and without doubt detached from the same specimen. M'Coy's remark that the corallites were upwards of 8 inches in length presupposes either that the holotype was originally longer or that he had other specimens as well.

The largest corallite is 8 mm. in diameter, with thirty-four major septa 2 mm. to 2·5 mm. long; and the smallest corallite is only 4 mm. in diameter. The minor septa are one-third the length of the major, *i. e.*, less than 1 mm.

In transverse sections of this and in most other sections of {*Diphyphyllum*} the major septa appear to end against a complete ring, which suggests an aulos, or an inner wall, but this is merely formed by the intersections of axial tabulæ. The character of the tabulæ is well seen in the longitudinal sections of the topotypes (Pl. VII. figs. 3 *b*, 4 *b*). They include two series of plates, of which the inner series are horizontally disposed, convex, and superposed one upon another, forming an axial column: they are unequally spaced, some being very close together, others 1·5 mm. apart. The outer tabulæ, which slope downwards and towards the periphery, occupy a very narrow area, and abut, on the one hand, against the down-bent margins of the inner tabulæ and, on the other, against the innermost dissepiments. Here and there, however, the wall of the axial column is broken by an inner tabula extending to the theca, instead of curving round to touch the tabula below. The dissepiments are small and strongly arched, but vary in size. There are usually two rows, seldom only one, sometimes three. In a corallite 6 mm. in diameter the axial tabulæ occupy 4 mm., and the outer tabulæ and dissepiments together 1 mm. on each side.

It is to be noted that an impersistent columella is often represented by spines on successive tabulæ, and that some specimens (*e. g.*, British Museum R. 4506) have the rudiments of an axial complex like that described in *Nemistium edmondsi* (Smith, 1928, pp. 116-7, pl. v. figs. 1-4), into which form "species" of {*Diphyphyllum*} imperceptibly merge.

Lithostrotion sp. {*Diphyphyllum gracile* (M'Coy)}.
(Pl. VII. figs. 5 & 6.)

Diphyphyllum gracile, M'Coy, 1851[2], p. 168; 1851, p. 88, text-figs. *d*, *e*, and *f* on p. 88.

Holotype.—Sedgwick Museum, Cambridge. Specimen 122 (Carboniferous). The Impure Limestone of Lowick, Northumberland.

This consists of part of a corallum, embedded in a piece of dark-coloured limestone 10 cm. × 7 cm. × 5 cm., from which a small piece has now been cut in order to provide the thin sections here figured.

The slender cylindrical corallites are erect and closely packed. Their diameter is usually rather more than 3 mm., but one or two—much bigger than the rest—are as much as 6 mm. There are about 20 major septa between 0·5 mm. and 1 mm. long. The minor septa are very short indeed, usually being less than one-fourth the length of the major, and thus hardly noticeable in many of the corallites. The axial tabulæ, which may be as much as 1 mm. apart and are fairly evenly spaced, are arranged as in the other forms of {*Diphyphyllum*}. They thus appear strongly arched, although their crest may be flat. They occupy an area 2 mm. in diameter, *i. e.*, two-thirds of the corallite; whilst the narrow peripheral area about 0·5 mm. wide is occupied mainly by the outer tabulæ, which are nearly horizontal but slope slightly downwards towards the periphery. Some dissepiments may be present, but these at most form merely a single row and are not persistent. A columella is sometimes represented by a series of short spines, which rise from successive tabulæ, but do not reach the tabula above.

On the whole, M'Coy's description is very accurate, but he evidently confused the outer tabulæ with the dissepiments. We have frequently noted corals intermediate in character between M'Coy's type of {*D. gracile*} and small columellate *Lithostrotion*—*L. junceum* (Fleming) as well as small forms of *L. irregulare* (Phillips).

Lithostrotion sp. {*Diphyphyllum fasciculatum* (Fleming)}. (Pl. VII. figs. 7 & 8.)

Caryophyllea fasciculata, Fleming, 1828, p. 509.

Non *Caryophyllia fasciculata*, Lamarck, 1816, p. 226 (Recent).

Non *Lithodendron fasciculatum*, Phillips, 1836, p. 202, pl. ii. figs. 16 & 17.

Non *Caryophyllia fasciculata*, de Koninck, 1842, p. 17, pl. D. figs. 5 *a–c*, pl. G. figs. 9 *a, b*.

Non *Lithodendron fasciculatum*, Keyserling, 1846, p. 170, pl. iii. figs. 2, 2 *a–b*.

Non *Diphyphyllum fasciculatum*, D'Orbigny, 1850, p. 159.

? *Lithodendron fasciculatum*, Portlock, 1843, p. 335.

Original description.—" Crowded, branched, round, nearly cylindrical, slightly flexuous, and about a quarter of an inch in diameter.—Madreporite, *Park.* Org. Rem. 51, t. vi. f. 8. —Madrepora cespitosa, *Mart.* Derb. t. 17, *Carboniferous Limestone.*"

Syntypes.—There are two specimens in the Fleming collection labelled "*Caryophyllea fasciculata*," namely 1870.14.374 and 1870.14.337. The first of these (1870.14.374) is here chosen as the lectotype. This is from Skate Craig, Dunbar.

Lectotype.—The specimen measures 18 cm. × 10 cm. × 5 cm.; the coral and matrix are light-coloured. The corallites, which have an average diameter about 5 mm., are crowded and rather flexuous. The structure is the same as that of the other three forms of *Diphyphyllum* here described. There are about twenty-four major septa about 1·5 mm. long; the minor septa attain only half, or less than half, this length. The axial tabulæ are approximately 3 mm. in diameter, and are generally nearly 1 mm. apart, but the intervals between them vary, sometimes being somewhat more than 1 mm. and sometimes much less. The outer tabulæ and the dissepiments together occupy 1 mm. on each side of the axial tabulæ. The dissepiments usually fill a narrower area than the outer tabulæ, and are typically arranged in one row only, but here and there there are two rows. The dissepimental vesicles contain much stereome.

It is possible that Fleming knew of Lamarck's *Caryophyllia fasciculata* when he named this coral, but we cannot assume this, for he makes no reference to Lamarck; and since his species belongs to an entirely different genus and class, Fleming's name may be used for those forms of {*Diphyphyllum*} that are intermediate in size between {*D. lateseptatum*} and {*D. gracile*}, and otherwise agree with his type of *Caryophyllum fasciculata.* The species should, therefore, be designated as *Lithostrotion* sp. {*Diphyphyllum fasciculatum* (Fleming)}.

Lithostrotion, Fleming, 1828, p. 508, genomorph {*Diphystrotion*, nov.}.

Genomorphotype: *Stylastræa inconferta*, Lonsdale, 1845, p. 621 pl. A. figs. 2, 2 *a–c*.

Diagnosis.—Cerioid *Lithostrotion* in which there is no columella, or one which is reduced to spines on successive tabulæ, and in which the tabulæ are slightly convex or flat and in most cases complete. The dissepimental tissue is typically coarse. Parricidal gemmation has not been observed.

Remarks.—{*Diphystrotion*} leads on to *Thysanophyllum*, Thomson (strictly interpreted by the genotype), which has a thoroughly lonsdaleoid border; but not to "*Thysanophyllum*" *vermiculare*, which is the corresponding development of the fasciculate {*Diphyphyllum*}.

Lithostrotion sp. {*Diphystrotion inconfertum* (Lonsdale)}. (Pl. VII. figs. 9–13.)

Stylastræa inconferta, Lonsdale, 1845, p. 621, pl. A. figs. 2, 2 *a–c*.

Holotype.—British Museum, specimen R. 17562, Kossatchi-Datchi, South of Miask, eastern side of Ural Chain (about 900 miles due E. of Moscow). There are isolated corallites and sections of parts of the same specimen separately numbered.

The specimen, which is 10 cm. long and 5·5 cm. × 4 cm. transversely, consists of a few easily separable prismatic corallites, the largest of which is about 10 mm. in diameter. Most of them are to some extent crushed and broken. The material is re-crystallized (and to some extent dolomitized); and the vesicular tissue is not completely filled by mineral calcite, although it contains much stereome. The epitheca is finely striated longitudinally and wrinkled transversely. This, and the general shape, is very well shown in Lonsdale's figure (pl. A. fig. 2).

In most of the corallites there are eighteen major septa, generally including one septum much longer than the rest, like that of *Thysanophyllum orientale*, Thomson. This counter-septum reaches beyond the axis, whilst the others only extend inwards 2 to 4 mm. The minor septa are very feebly developed, few being as much as 1 mm. In most cases the septa reach the epitheca, but here and there—on one side or another of a particular corallite—they end peripherally against a large dissepiment. The septa are thin and, seen in transverse section, rather crooked, particularly the long counter-septum. The sides of the septa, where exposed by longitudinal fracture *, are corrugated by sinuous folds, which slope downwards axially and are themselves transversed at right angles by very fine and rather faint corrugations.

There is no continuous columella, but some axial structures recalling those in *Nemistium edmondsi* † may occur on successive tabulæ.

The tabulæ, which may or may not be complete, are convex distally, reach the theca, and are not differentiated into distinct series, as in the forms of {*Diphyphyllum*} which we have described. They are unequally distributed, and may be as much as 2 mm. apart, although the average distance between them is less than 1 mm.

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* This particular specimen breaks longitudinally in an unusual manner; namely, along the sides of the septa (which are thus exposed to view), owing to some incoherence between the septa and the matrix which fills the vesicular tissue between them.

† Smith, 1928, pp. 112–120.

The dissepiments are large, and form only a single, or at most a double, row of strongly-arched plates. The width of the dissepimental area is about the radius of the corallite.

Lithostrotion sp. {*Diphystrotion kendalense,* new form}. (Pl. VII. figs. 14 & 15.)

"*Stylastræa basaltiformis* (Phill. sp.)," M'Coy, 1851, p. 107, no figure.

Holotype.—Sedgwick Museum, Cambridge. Specimen 130. Specimens 131 and 133 parts of the same piece of coral. Carboniferous Limestone, Kendal.

The holotype is a little over 25 cm. in length, and consists of unusually long, remarkably straight, easily separable corallites, some of which run the entire length of the specimen, and most of them nearly as far. The material is well preserved, but appears to be a little dolomitized, and here and there the interstices of the coral are free from mineral matter. As in *S. inconferta*, the corallites are lightly striated and transversely wrinkled, and attain a maximum diameter of about 10 cm., but have about twenty-five major septa, which are not more than 3 to 4 mm. long. The septa reach the epitheca, but the major septa are very often interrupted by the large dissepiments, and appear discontinuous in transverse section. For the most part the axial region is quite free of longitudinal tissue. The tabulæ, which are nearly all complete, are flat or sagging, but bend downwards near their periphery. The dissepiments vary considerably in size, some being distinctly large and others quite small. The dissepimental area occupies about half the radius of the corallite.

{*D. kendalense*} closely resembles {*D. inconfertum*}, but shows some small differences, as may be seen from the description and in the figures. The flatter tabulæ, almost entire absence of any axial structure, and greater development of dissepimental tissue are the chief. The septa, moreover, do not show the corrugations mentioned in Lonsdale's form.

"*Stylastræa basaltiformis* (Phill. sp.)," M'Coy, as we have seen, is a diphymorph, and is not *Astrea basaltiformis*, Conybeare & W. Phillips, which was founded on Lhwyd's figure already quoted (p. 178). It is therefore necessary to re-name M'Coy's form, and, since we consider {*Diphystrotion*} to be a genomorph of *Lithostrotion*, we name it *Lithostrotion* sp. {*Diphystrotion kendalense*}.

It is not possible to tell from John Phillip's figure or his description of "*Cyathophyllum basaltiforme*" whether the form is, or is not, identical with M'Coy's.

AULOPHYLLUM, Edwards & Haime, 1850, p. lxx.

Genotype: *Clisiophyllum prolapsum*, M'Coy, 1849, p. 3; 1851, p. 95, pl. 3 *c.* figs. 5, 5 *a.* Carboniferous Limestone, Derbyshire. = *Turbinolia fungites*, Fleming, 1828, p. 510. = *Fungites*, Ure, 1793, p. 327, pl. xx. fig. 6.

Diagnosis.—Simple, trochoid Rugose corals, often of large size, with a compact well-defined central column, which, seen in transverse section, has a cuspidate outline and is built up of closely-packed vertical and horizontal elements. The major septa do not usually extend quite to the axial complex. The tabulæ are small and arched, and slope down towards the periphery. There is a well-developed peripheral zone of numerous small dissepiments.

Remarks.—*Aulophyllum* differs from all other Clisiophyllids in having the number of radial lamellæ within the central column greater than the number of septa, and from most in having no axial plates. In other respects it agrees with the typical Clisiophyllids.

Aulophyllum fungites (Fleming).

Turbinolia Fungites, J. Fleming, 1828, p. 510.
Aulophyllum fungites (Fleming), Edwards & Haime, 1851, p. 413; 1852, p. 188.

Fleming describes the species, which is the genotype of *Aulophyllum*, as: "Inversely conical, lengthened; more or less bent; longitudinally striated, with irregular transverse wrinkles; star concave, with a large central axis. Fungites, *Ure*, Ruth. 327, lxx. fig. 6.—In *Carboniferous Limestone*, common; frequently termed *Rams' horns*." Eight syntypes (Specimens 1870.14.428) remain in Fleming's collection, most of them being typical material and conspecific with D. Ure's specimen of *Fungites* (1793, p. 327, p. xx, fig. 6), to which Fleming refers, and which has been virtually chosen as the lectotype; although in the detailed description and summary of the literature of *Aulophyllum fungites* by S. Smith (1913, pp. 51–77, pls. v.–ix.), and in Gregory's later remarks (1917, pp. 223–4), this was not definitely stated. In order to avoid any future ambiguity, we hereby choose Ure's figured specimen of *Fungites* as the lectotype of *Turbinolia fungites*, Fleming.

It may be added that Thomson (1882, p. 481) referred Ure's specimen of *Fungites* (of which he cut sections) to *Cyclophyllum*, Duncan & Thomson, 1867, and figured it as *C. fungites*. But it has been shown conclusively that *Cyclophyllum*, Duncan & Thomson, is identical with *Aulophyllum* (see S. Smith, 1913, pp. 54–55, and Gregory, 1917, pp. 223–4). It may also be pointed out that in 1867 Duncan and Thomson founded *Cyclophyllum* on two syntypes, namely, *Aulophyllum fungites* (*Turbinolia fungites*, Fleming) and *A. bowerbanki*, Edwards & Haime, of which the former was regarded by Edwards and Haime as conspecific with the genotype of *Aulophyllum*; and we consider that the two forms are identical.

Gregory (1917, p. 273) chose *A. bowerbanki*, Edwards & Haime, as genolectotype of *Aulophyllum*, but Edwards and Haime (1850, p. lxx) had already given *Clisiophyllum prolapsum* as the genoholotype.

CHÆTETES, G. Fischer von Waldheim, 1830, sig. *d*, 4; 1837 (second edition), p. 160.

Genosyntypes: *Chætetes radians*, G. Fischer v. Waldheim, 1830, sig. *d*, 4.
Chætetes dilatata, " " " "
Chætetes cylindrica, " " " "
Chætetes incrustans, " " " sig. *e*, 1.
Chætetes gigantea, " " " "
Chætetes jubata, " " " "

Genolectotype: *Chætetes radians*, G. Fischer von Waldheim, 1830, sig. *d*, 4: 1837, p. 160, pl. xxxvi. fig. 3 (referred to in text as fig. 6), Carboniferous. Miatchkova (14 miles S.W. of Moscou), Russia. See H. M. Edwards and J. Haime, 1850, p. lxi.

Diagnosis.—Cerioid or meandroid Tabulate corals, which form tumular or stratiform masses, and have small corallites with thin, complete, horizontal tabulæ, but no septa, and probably no mural pores. The walls separating the individual corallites are often incompletely formed, and may appear [illegible] y [illegible], and [illegible]

Remarks.—[illegible] Waldheim's descriptions of the genosyntypes of *Chætetes* are in themselves too inaccurate for diagnostic purposes, nevertheless the figures clearly and unmistakably show that the corals belong to the same genus, and probably all to the same species, as the coral described and figured by Lonsdale, 1845, p. 595, pl. A. figs. 9, [illegible] *radians*, from Borovitchi etc., Government [illegible] Lonsdale's figured specimen is in the British [illegible] *Chætetes radians* is interpreted by [illegible] conspecific with *Favosites septosus*, Fleming. [illegible] Lonsdale's specimen the tabulæ are grouped [illegible] wide apart and near together, [illegible] are fairly equally distributed, [illegible] observed both conditions in British and Russian specimens, and consider the distribution of tabulæ to be due to environmental conditions, and not to be a congenital character. The walls are thicker in Lonsdale's specimen than in Fleming's, and in consequence of this the corallites of Lonsdale's specimen have a much more rounded interior.

Fischer von Waldheim's statement that the tubes were without diaphragms can be explained, either by the fact that the tabulæ had been destroyed by silification, which, he says, affected many of his specimens, or that he did not notice the thin and distant tabulæ on its broken surface.

Both Edwards and Haime (1851, pp. 259–263; 1852, pp. 157–8) and Thomson (1882, p. 201) regarded *Chætetes radians*, Fischer von Waldheim, and *Favosites septosus*, Fleming, as distinct species, and even as distinct genera, on the grounds that the latter had, and the former had not, mural pores. Nicholson and Etheridge (1877, pp. 366–367), on the other hand, could detect pores in neither species, and considered the two forms to be at least congeneric. As to the mural pores, we have not been able to detect them ourselves, but Thomson claims to have done so in specimens from Scotland (1882, p. 197). If present, they are necessarily very small, and would easily be obliterated in the process of mineralization; whereas those of the genotype of *Alveolites* are large.

Two clear trends are manifest in *Chætetes*, namely, a thickening of the wall and the development of such meandroid colonies as are exhibited in an exaggerated degree by the form from Ireland recently described and figured by Smyth (1925, pp. 319–320, pls. xiv., xv.).

Chætetes radians, Fischer von Waldheim, *interp.* Lonsdale.

Chætetes radians, Fischer von Waldheim; Lonsdale, 1845, p. 595, pl. A. figs. 9, 9 *a*. This is probably *Chætetes radians*, Fischer von Waldheim, 1837, p. 160, pl. xxxvi. fig. 3 (*non* fig. 6 as in text): it is certainly *Favosites septosus*, Fleming

Lonsdale's material.—Specimens from Kaluga (Government of Kaluga, 100 miles S.S.E. of Moscow); Borovitchi (Government of Novgorod, 240 miles N.E. of Moscow) and Vitegra, on S.W. side of Lake Onega (Government of Olonetz, nearly 400 miles N. by E. of Moscow).

Neotype.—On the assumption that Fischer von Waldheim's material is lost, we select Lonsdale's figured specimen, British Museum 26356, Carboniferous, Kaluga or Vitegra (old label reads Kaluga and Vitegra), as neotype.

The specimen, 10 cm. high, 6·5 cm. wide, is part of a large tumular colony of radiating, separable, prismatic corallites.

The corallites are fairly regular in section, and are almost 0·5 mm. in diameter. They have thick walls, rounded angles, and very thin tabulæ, which may be as much as 5 or 6 mm. distant or may be very close together. The tabulæ occur at the same level in neighbouring corallites, and form continuous platforms. Wide bands of widely-separated tabular platforms alternate regularly with narrow bands of closely-packed platforms, as shown by Lonsdale's fig. 9. It should be added, however, that the widely-separated tabulæ of one part of the corallum may approximate in another part of the mass if the individual bands are followed far enough. The neotype also exhibits very clearly the incomplete walls mentioned in our diagnosis and well illustrated by Lonsdale in fig. 9 *a*.

Chætetes septosus (Fleming).
(Pl. VIII. fig. 1.)

Favosites septosus, Fleming, 1828, p. 529.
Alveolites septosa, Edwards & Haime, 1851, p. 259; 1852, p. 157, et auctt.

Holotype.—Specimen 1870.14.123, Fleming Collection, Royal Scottish Museum, Edinburgh. Carboniferous Limestone. No locality.

The black holotype exactly answers Fleming's description: "Hemispherical, nearly 2 inches in diameter, the tubes radiating from the centre irregularly, divided internally by simple transverse plates.—*Carboniferous Limestone*." It is a small colony, 7 cm. in diameter and 4 cm. high. The base is a broken surface. The corallum has been cut longitudinally, and the face of each half roughly polished.

The corallites radiate from a centre, and the colony has the appearance, characteristic of *Chætetes*, of having been built up of several concentric layers. The corallites are prismatic and fairly uniform in size, averaging 0·75 mm. in diameter. The tabulæ are complete, horizontal, and fairly equally distributed at intervals of about 0·5 mm. An incomplete wall is present in many of the corallites, and a slight tendency to assume the meandrine condition is seen locally.

Edwards and Haime's description (1852, p. 157), based on material from various localities, thus agrees very closely with the type.

J. Thomson's remarks upon "*Alveolites septosa*" (1882, p. 205; 1883, p. 344) more fully describe the form, and are perhaps even more accurate in detail, but we disagree with his statements that the corallites are from 5 to 11 lines long, since they may attain a length of several centimetres if not interrupted by the superposition of new growth upon old, which is frequent and referred to by Edwards and Haime (1852, p. 157).

Chætetes depressus (Fleming). (Pl. VIII. fig. 2.)

Favosites depressus, Fleming, 1828, p. 529.
Alveolites depressa, Edwards & Haime, 1851, p. 260; 1852, p. 158, et auctt.

Holotype.—Specimen 1870.14.122, Fleming Collection, Royal Scottish Museum, Edinburgh. Carboniferous Limestone. No locality.

The original description reads:—"An extended plate about an inch in height, tubes vertical, rather smaller than the preceding, and less divided.—*Carboniferous Limestone*," and this agrees so closely with specimen 1870.14.122 that there can be little doubt that it is that which Fleming had in mind when he wrote these words. It is a flat piece of black limestone, 8 cm. × 2·5 cm., enclosing a thin band of coral 2·5 cm. in thickness. The small parallel corallites are very well exposed on the weathered surface, where the coral stands out white (although crossed by numerous thin black lines) from the dark matrix, and the separable character of the "tubes" is clearly demonstrated.

The corallites are sub-prismatic, nearly cylindrical, and average less than 0·2 mm. in diameter. As far as one is able to judge, the tabulæ are unevenly distributed, in some places lying close together, but in others far apart.

Chætetes depressus is easily distinguished from *Ch. septosus* by its very much smaller corallites, which are only about one-fourth the diameter of the large form. Whilst both species may form extensive stratiform growths, that habit is usual in *C. depressus*, whereas a tumiform shape is more general in *C. septosus*.

ALVEOLITES, Lamarck, 1801, p. 375.

Genosyntypes: *Alveolites escharoides*, Lamarck, 1801, p. 376 (l'astroïte de Guettard, 1770, p. 499; pl. xlv. fig. 1).
Alveolites suborbicularis, Lamarck, 1801, p. 376 [Devonian, neighbourhood of Dusseldorf].

Genolectotype: *Alveolites spongites*, Steininger, 1831; 1834, p. 334, pl. xx. figs. 4, 4 *a–c*. = *Calamopora spongites*, var. *tuberosa*, Goldfuss, 1826, p. 80, pl. xxviii. figs. 1 *a*–1 *e*. See Edwards & Haime, 1850, pl. lxi. = *Alveolites suborbicularis*, Lamarck.

Diagnosis.—Massive tabulate corals, which form large colonies built up of superposed layers enwrapping some nucleus. The corallites are small, very oblique, more or less triangular in section, and have moderately thick walls, perforated by a few large mural pores. The septa may be altogether suppressed, but are typically represented by a single septum on the lower lip of the very oblique calice.

Remarks.—The characters distinguishing *Alveolites* from *Chætetes* have been thoroughly discussed by Nicholson and Etheridge, 1877, and again by Nicholson, 1879, pp. 117–125 and 260–266. The form of the calice and the solitary septa are well illustrated by Goldfuss's figure (1826, pl. xxviii. fig. 1 *c*). The young corallites arise at the angles between the older ones.

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EXPLANATION OF THE PLATES.

Plate VII.

Figs. 1 & 2. *Lithostrotion* sp. {*Diphyphyllum lateseptatum* M'Coy}. Holotype. Sedgwick Museum, Cambridge, No. 123. Lower Carboniferous, [Upper Grey Limestone ?, Hafod-y-Calch], Corwen, Merionethshire.

Fig. 1. Transverse section, × 1·5.

Fig. 2. Longitudinal section, exposed on face of specimen. Nat. size.

Figs. 3 & 4. The same. Topotypes. British Museum, Morton Collection R. 27243 and R. 27244. Lower Carboniferous, Upper Grey Limestone, Hafod-y-Calch, Corwen.

Figs. 3 *a*, 3 *b*. Transverse and longitudinal sections of R. 27243. × 2.

Figs. 4 *a*, 4 *b*. Transverse and longitudinal sections of R. 27244. × 2.

Figs. 5 & 6. *Lithostrotion* sp. {*Diphyphyllum gracile*, M'Coy}. Holotype. Sedgwick Museum, No. 122. Lower Carboniferous, "impure Limestone." Lowick, Northumberland.

Fig. 5. Longitudinal section. × 1·5.

Fig. 6. Tranverse section, × 1·5 (the detached corallite is much larger than the rest).

Figs. 7 & 8. *Lithostrotion* sp. {*Diphyphyllum fasciculatum* (Fleming)}. *Caryophyllia fasciculata*, Fleming. Lectotype. Royal Scottish Museum, Edinburgh. Lower Carboniferous. Skale Craig, Dunbar.

Fig. 7. Longitudinal section. × 2.

Fig. 8. Transverse section. × 2.

Figs. 9–13. *Lithostrotion* sp. {*Diphystrotion inconfertum* (Lonsdale)}. =*Stylastræa inconferta*, Lonsdale. Holotype. British Museum R. 17562. Lower Carboniferous. Kossatchi-Datchi, south of Miask, eastern side of the Ural Chain.

Figs. 9, 10, & 11. Transverse sections, R. 17566 (figs. 9, 10), R. 17576. × 2.

Figs. 12 & 13. Longitudinal sections, R. 17576, R. 17577. × 2.

Figs. 14 & 15. *Lithostrotion* sp. {*Diphystrotion kendalense*, new form}. = "*Stylastræa basaltiformis* (Phill.)," M'Coy. Sedgwick Museum, No. 131. Lower Carboniferous. Kendal, Westmorland.

Fig. 14. Longitudinal section. × 2.

Fig. 15. Transverse section. × 2.

PLATE VIII.

Fig. 1. *Chætetes septosus* (Fleming) = *Favosites septosus*, Fleming. Lectotype (? holotype). Royal Scottish Museum, Edinburgh, Fleming Collection, No. 1870.14.123. Lower Carboniferous (Scotland ?). × 3·5.

Fig. 2. *Chætetes depressus* (Fleming) = *Favosites depressus*, Fleming. Holotype. Royal Scottish Museum, Fleming Collection, No. 1870.14.122. Lower Carboniferous (Scotland ?). × 3·5.

XIV.—*Thysanoptera from Africa.*

By DUDLEY MOULTON, San Francisco, California.

THIS paper includes a record of various species of the Terebrantia which have been received principally from Mr. Frederick Laing of the British Museum, London, who has forwarded collections made by Mr. R. E. Turner. Collections from Messrs. A. Cuthbertson and Rupert W. Jack, Rhodesia, and Mr. A. W. J. Pomeroy, Gold Coast, are also included. Another paper will be offered shortly on those species belonging to the Tubulifera. I wish to express my sincere appreciation to these men, who, by their cooperation, have made this paper possible.

Superfamily **ÆOLOTHRIPOIDEA**, Hood.

Family **Orothripidæ**, Bagn., 1926.

AUDIOTHRIPS, gen. nov.

Antennæ 9-segmented, ovipositor upturned and closely related to *Erythrothrips*, Moulton, except that in this new genus the maxillary palpus has five segments instead of eight, and the sense-areas on the third and fourth antennal segments are elongate, extending the full length of the segments, while in *Erythrothrips* they are much shorter and occupy a position only in the distal ends of the segments. This genus approaches *Franklinothrips*, Back, in the great length of the sense-areas and by the elongate third antennal segment, which, however, is much shorter and broader in *Audiothrips* than in *Franklinothrips*.

Genotype, *Audiothrips perplexus*, sp. n.

1. *Audiothrips perplexus*, sp. n.

Female holotype.—Colour of body and legs uniformly deep brown. Antennal segments 1, basal three-fourths of 2 and 4 to 9 concolorous with head; tip of 2 and all of 3 whitish, 4 whitish at base gradually shading to brown at tip. Wings whitish with a dark longitudinal band extending from extreme base, including scale, to tip. This brown band is somewhat narrower in basal third and wider in middle third.

Total body-length 2·5 mm.; head, length ·23 mm., width ·23 mm.; prothorax, length ·16 mm., width ·23 mm.; pterothorax, width ·35 mm.; greatest width of abdomen ·43 mm. Antennæ: length (width) i. 45 (42), ii. 51 (33), iii. 174 (27), iv. 120 (27), v. 60 (24), vi. 45 (24), vii. 48 (21); viii. 24; ix. 12; total length 600 μ.

Head subquadrate; cheeks slightly arched, without conspicuous spines. Eyes extending posteriorly on ventral side. Ocelli normal. Maxillary palpi geniculate, with five segments, although the sutures between the second and third and third and fourth are more or less indistinct. Labial palpi 4-segmented, basal joint very small. Antenna with nine segments, 2·6 times as long as head, segment 3 elongate-cylindrical, ·8 as long as head and 6·5 times as long as wide.

Segment 4 also elongate-cylindrical and ·75 as long as segment 3; 5, 6, and 7 almost subequal, 8 and 9 small, conical, and closely joined to 7. Sense-area on segment 3 narrow, slightly enlarged, and bent at distal end, extending along outer side to near extreme base; sense-area on segment 4 similarly shaped, and also extending to extreme base of segment.

Prothorax small, about as wide as head and ·7 as long, without conspicuous markings or spines. Pterothorax with sides evenly arched. Legs long and slender. Fore femora only very slightly larger than middle and hind femora. Each fore tarsus with a hook-shaped tooth. Wings fully developed, with ring-vein, two longitudinal veins, and four cross-veins.

Abdomen elongate-ovate, with prominent spines only on ninth and tenth segments.

This species resembles *Erythrothrips arizonæ*, Moulton, in shape of body and colour of wings. The third antennal segment resembles *Æolothrips nasturtii*, Jones, but is somewhat longer. It is difficult to state with certainty whether the sutures between the second and third and the third and fourth segments of maxillary palpi are complete in the holotype; they are distinct in the paratype. The sense-areas of third and fourth antennal segments extend over the entire length of the segments as in *Franklinothrips*.

Type material.—Female holotype (Moulton no. 2838) and one ♀ paratype (no. 2831), taken from an unknown host, iii. 1927 (*R. E. Turner*). Holotype deposited with British Museum, paratype in author's collection.

Type-locality.—Orange Free State, South Africa.

Family Æolothripidæ, Uzel, 1895.

2. *Æolothrips brevicornis*, Bagnall.

One ♀ specimen taken at Mossel Bay, Cape Province, viii. 1924 (Moulton no. 2845); one ♀ at Goerge, Cape Province, vii. 1920 (no. 2855); one ♀ taken at Drakensberg, Natal, in 1926, elevation 6500 feet (*R. E. Turner*) (no. 2874). Specimens nos. 2855 and 2874 deposited with the British Museum, no. 2845 in author's collection.

3. *Æolothrips scabiosatibia*, sp. n.

Female holotype.—Colour uniformly dark brown, except segment 3 of antenna, extreme tip of 2, tarsi, and the median portion of fore tibiæ, which are yellowish. Fore wings with two dark cross-bands, hind wings without noticeable colouring.

Total body-length 1·66 mm. (somewhat distended); head, length ·16 mm. (head-length of paratype ·15 mm., width ·18 mm.); prothorax, length ·15 mm., width ·25 mm. Antennæ: length (width) i. 24 (30), ii. 48 (27), iii. 75 (24), iv. 60 (27), v. 60 (27), vi–ix. combined 39 μ; total length 316 μ.

This species is closely related to *Æolothrips brunicornis*, Bagnall, in that each fore wing has two dark cross-bands, typical of the *A. fasciatus*-group, antennal segments 6–9 are subequal and together, like *A. brevicornis*, are much shorter than 5, segments 4 and 5 are subequal, and about four-fifths as long as segment 3. Entire antenna is moderately stout and approximately twice as long as head; sense-areas on segments 3 and 4 moderately broad, extending two-thirds the length of the segments. This species is especially characterized by the unusually roughened fore tibiæ, which are normally spiny on the dorsal side, but on the ventral side each spine arises from the side of a small wart or tubercle, which makes the surface of the tibiæ extremely rough. The spines of the middle and hind tibiæ are normal; unfortunately the fore tibiæ are broken from the second paratype, but after measurement and comparison I have referred the second paratype to this species rather than to *brevicornis*.

Type-material.—Female holotype (Moulton no. 2905); two ♀ paratypes (nos. 2902 and 2904), collected from an unknown host-plant in iv. 1925 (*R. E. Turner*). Holotype and one paratype deposited with British Museum, one paratype in author's collection.

Type-locality.—Ceres, Cape Province, South Africa.

4. *Rhiphidothrips turneri*, sp. n.

Male holotype.—Colour uniformly dark brown except tips of second and third antennal segments, which are lighter (unfortunately the antenna is broken off beyond the second segment, but the third and fourth segments of one antenna are present, though detached; the fore and middle pair of legs are also lost). Hind legs uniformly dark brown like the body. Wings whitish in basal quarter, with uniformly dark brown band across the second and third quarters, a white band across the first half of the last quarter, with tip of wing brown like the median portion, posterior pair of wings banded like the anterior pair but less distinctly.

Total body-length 1·33 mm. Antennæ: length (width) i. 36 (36), ii. 45 (30), iii. 105 (30), iv. 105 (27) μ.

Head somewhat longer than wide; cheeks straight, without prominent spines.

Prothorax only slightly wider than head. Pterothorax elongate-ovate. Wings clearly narrowed in basal quarter, gradually becoming wider to near middle, distal half of wing with sides almost parallel. Sternites without depressions.

Type-material.—Male allotype (Moulton no. 2835), taken on an unknown host-plant, 20.iii.1927 (*R. E. Turner*). Holotype deposited with the British Museum.

Type-locality.—Harrismith, Orange Free State, South Africa.

The single specimen before me is distinct from other species of the genus by its broadly banded wings approaching only *R. cinctus*, Hood, from Queensland, Australia, but differing from this by the much broader median band. This species is also interesting because it is the first of the genus recorded from South Africa.

Family **Franklinothripidæ**, Bagnall, 1926.

5. *Franklinothrips megalops*, Trybom.

Nine ♀ specimens taken at Mossel Bay, Cape Province, South Africa, iv.1921 and ii. 1922 (*R. E. Turner*).

Superfamily **THRIPOIDEA**, Hood.

Family **Thripidæ**, Uzel, 1895.

Subfamily *HELIOTHRIPINÆ*, Karny.

6. *Hercothrips bicinctus*, Bagnall.

One ♀ specimen taken at Eshowe, Zululand, South Africa, v.1926 (*R. E. Turner*) (Moulton no. 2869).

For diagnosis of this genus see Hood, 'Psyche,' vol. xxxiv. no. 6, Dec. 1927.

Subfamily *SERICOTHRIPINÆ*, Karny.

7. *Sericothrips occipitalis*, Hood.

Eight female and two male specimens collected from bean-foliage, 10.iv.1922 (*A. Cuthbertson*), at the Agricultural Experiment Station, Salisbury, South Africa.

The specimens from which this species was described were found at Ibadan, Southern Nigeria, and the present record extends its distribution into South Africa.

Two specimens deposited with British Museum (Moulton, no. 1640).

8. *Scirtothrips pomeroyi*, sp. n.

Female holotype.—Colour uniformly light yellow except wings, antennal segments 1 and 3, which are whitish yellow, and distal two-thirds of 6, 7, and 8, which are greyish brown; 4 and 5 also have a shading of greyish brown on upper and lower sides of distal two-thirds. Crescents of ocelli orange-red.

Total body-length ·916 mm.; head, length ·069 mm., width across at eyes ·10 mm.; prothorax, length ·144 mm., greatest width across posterior fourth ·135 mm.; pterothorax, width ·168 mm.; abdomen, width ·21 mm. Antennæ: length (width) i. 15 (24), ii. 30 (22), iii. 33 (18), iv. 33 (18), v. 30 (18), vi. 36 (15), vii. 9, viii. 10; total length 195 μ.

Head clearly transverse, rounded in front; cheeks short, slightly converging toward the posterior. Interocellar spines small and placed almost directly in front of posterior ocelli, other head-spines inconspicuous. Eyes large, occupying more than half the length of the head. Ocelli fully developed. Mouth-cone long, pointed, reaching four-fifths across prosternum. Maxillary palpi 3-segmented. Antenna 2·8 times as long as head, segment 3 broadly clavate, 4 and 5 subovate, each with a small pedicel.

Prothorax slightly longer than greatest width and slightly more than twice as long as head, sides gradually diverging to near posterior fourth, from there converging to form broadly rounded angles. Spines on anterior angles vestigial, with a single prominent, though short, spine on each posterior angle, and a series of four small ones along posterior margin on either side. Pterothorax only slightly wider than prothorax. Sides of mesothorax broadly rounded, of metathorax straight and almost parallel. Legs normal. Wings fully developed, fore longitudinal vein fairly distinct. Spines as follows:—3—3 at base and three evenly placed over distal half, the first one being near the centre of the wing; hind vein very indistinct, but with three scattered bristles near centre of wing and one near tip where vein should be.

Abdomen elongate-ovate, with last three segments rather pointed, conical, without pubescence. Posterior margin of eighth tergite without cone. Longest spines on segments 9 and 10 approximately 75 μ, segment 10 with dorsal suture.

takes place with liberation of methane, and not of methyl chloride as stated by Beyer.

In the presence of iodine, phorone and mesityl oxide yield acetone, unchanged phorone, and acetoneanil. In the absence of iodine, condensation does not appear to occur. Under the influence of iodine and water, phorone does not appear to yield acetone. H. W.

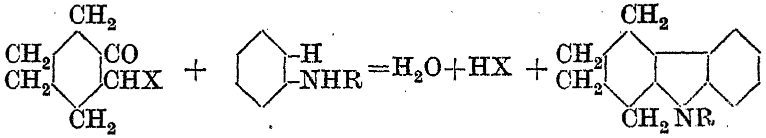
Amino-alcohols of the Quinoline Series. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 98482, 98712, and 98713; from *Chem. Zentr.*, 1923, iv, 829—830; cf. A., 1923, i, 148, 149).—6-Ethoxy-2-phenyl-4-quinolyl methyl ketone is halogenated in the methyl group and the resultant halogen derivative allowed to react with dimethylamine, diethylamine, or piperidine. The *N*-substituted 6-ethoxy-2-phenyl-4-quinolylamino-ethanone thereby obtained is then reduced to the corresponding aminoalcohol. 6-*Ethoxy*-2-*phenyl*-4-*quinolyl methyl ketone* forms yellow crystals, m. p. 107°; the *hydrochloride*, yellow crystals, has m. p. about 220° (decomp.). It is obtained by condensation of ethyl 6-ethoxy-2-phenylquinoline-4-carboxylate with ethyl acetate and elimination of carbon dioxide from the *ethyl* 6-*ethoxy*-2-*phenylquinoline*-4-*acetate*, m. p. 98—99°, thereby formed, or from 4-cyano-6-ethoxy-2-phenylquinoline by the Grignard reaction. By acting on the above-mentioned ketone with bromine in hydrobromic acid solution, 6-*ethoxy*-2-*phenyl*-4-*quinolyl bromomethyl ketone hydrochloride*, yellow crystals, m. p. 207° (decomp.), is obtained; the free *ketone* forms yellow crystals, m. p. 129°. By acting on the bromomethyl ketone with dimethylamine, 6-*ethoxy*-2-*phenyl*-4-*quinolyl dimethylaminomethyl ketone*, $OEt \cdot C_9NH_4Ph \cdot CO \cdot CH_2 \cdot NMe_2$, is obtained as the *hydrobromide*, yellow crystals, m. p. 230° (decomp.). The latter by reduction with hydrogen in the presence of a catalyst gives 6-*ethoxy*-2-*phenylquinolyl*-4-*dimethylaminoethanol*,

$$OEt \cdot C_9NH_4Ph \cdot CH(OH) \cdot CH_2 \cdot NMe_2,$$

which forms colourless, rosette-like needles, m. p. 95°; the *dihydrochloride* forms light yellow crystals, m. p. about 210° (decomp.). 6-*Ethoxy*-2-*phenyl*-4-*quinolyl diethylaminomethyl ketone monohydrobromide*, yellow crystals, m. p. about 210° (decomp.), 6-*ethoxy*-2-*phenyl*-4-*quinolyl piperidinomethyl ketone*, a yellow powder, m. p. 82° (indef.), the *hydrochloride*, m. p. about 260° (decomp.), and the *hydrobromide*, m. p. 235—240° (decomp.), of the latter are similarly obtained. The corresponding amino-alcohols are obtained by reduction. 6-*Ethoxy*-2-*phenyl*-4-*quinolyldiethylaminoethanol* forms crystals, m. p. 89° after softening; the *dihydrochloride*, yellow crystals, has m. p. 205°. 6-*Ethoxy*-2-*phenyl*-4-*quinolylpiperidinoethanol* forms colourless crystals, m. p. 110°; the *dihydrochloride*, yellow crystals, has m. p. 218°. G. W. R.

Preparation of a 2-Phenylquinolinedicarboxylic Acid. NEUMANN & Co. and J. ZELTNER (D.R.-P. 373285; from *Chem. Zentr.*, 1923, iv, 664—665).—Acetophenone-*o*-carboxylic acid, prepared, for example, from phthalic anhydride, acetic anhydride, and potassium acetate, is condensed with isatin by heating in the presence of potassium hydroxide solution at 100°. On acidifying, 2-*phenylquinoline*-4 : 7-*dicarboxylic acid* is obtained; it is a yellow, crystalline powder, m. p. 200°. G. W. R.

Preparation of Tetrahydrocarbazoles. CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (D.R.-P. 374098; from *Chem. Zentr.*, 1923, iv, 724).—2-Halogen*cyclo*hexanones are condensed with primary or secondary aromatic amines, unsubstituted in the ortho-position to the amino-group. The reaction takes place in the presence of such basic substances as potassium carbonate or anhydrous potassium acetate, and is represented by



The following compounds are mentioned: tetrahydrocarbazole, from aniline and chloro*cyclo*hexanone; 3-*methyltetrahydrocarbazole*, m. p. 142°, from *o*-toluidine and chloro*cyclo*hexanone; 1-*methyltetrahydrocarbazole*, m. p. 98°, from *p*-toluidine and chloro*cyclo*hexanone; N-*ethyltetrahydrocarbazole*, a viscous oil, b. p. 220°/40 mm., from ethylaniline and 1 : 2-chloro*cyclo*hexanone. G. W. R.

Preparation of Aromatic α-Ketonic Acids. R. SÖDERQUIST (*Svensk Kem. Tidskr.*, 1922, **34**, 189—192; from *Chem. Zentr.*, 1923, iii, 1082—1083).—Aromatic α-ketonic acids are prepared by condensation of aldehydes with 4-oxo-2-thio-3-phenyloxazolidine. After oxidation and fission of the substituted oxazolidine ring, aromatic α-ketonic acids are obtained together with phenyl thiocarbimide. The condensation proceeds readily in acetic anhydride solution in the presence of anhydrous sodium acetate. Fission of the aryldihydroxyoxazolidines obtained by oxidation, takes place at the ordinary temperature on treatment with sodium ethoxide. The compounds may be separated by fractionation or by way of their hydrogen sulphite compounds. Anhydro-acids are also obtained from the elimination of a molecule of water from two ketonic acid molecules. 4-*Oxo*-2-*thio*-3-*phenyl*-5-*benzylideneoxazolidine*, from benzaldehyde and 4-oxo-2-thio-3-phenyloxazolidine, has m. p. 185—185·5°. On oxidation, it yields 2 : 4-*dihydroxy*-3-*phenyl*-5-*benzylideneoxazolidine*, m. p. 238—239°, whilst among the products of reaction with sodium ethoxide is phenylpyruvic acid. Other compounds mentioned are: 4-*oxo*-2-*thio*-3-*phenyl*-5-o-*chlorobenzylideneoxazolidine*, fine thread-like or prismatic crystals, m. p. 141·5°; 2 : 4-*dihydroxy*-3-*phenyl*-5-o-*chlorobenzylideneoxazolidine*, m. p. 152°; o-*chlorophenylpyruvic acid*, colourless leaflets, m. p. 145° (m. p. 152—152·5° when heated quickly); *semicarbazone* of the latter, m. p. 167·5°; *phenylhydrazone*, m. p. 141°; 4-*oxo*-2-*thio*-3-*phenyl*-5-m-*chlorobenzylideneoxazolidine*, light yellow prisms, m. p. 192°; m-*chlorophenylpyruvic acid*, prisms; semicarbazone of the latter, m. p. 176°; *phenylhydrazone*, m. p. 141°; 4-*oxo*-2-*thio*-3-*phenyl*-5-p-*chlorobenzylideneoxazolidine*, m. p. 237—237·5°; p-*chlorophenylpyruvic acid*, platelets; *semicarbazone* of the latter,

m. p. 184°; *phenylhydrazone*, m. p. 164°; *4-oxo-2-thio-3-phenyl-5-(3′ : 4′)methylenedioxybenzylideneoxazolidine*, m. p. 240° 2 : 4-*methylenedioxyphenylpyruvic acid*, colourless leaflets; *semicarbazone* of the latter, m. p. 197°; *phenylhydrazone*, m. p. 144° 4-*oxo-2-thio-3-phenyl-5-*m-*nitrobenzylideneoxazolidine*, m. p. 207° 4-*oxo-2-thio-3-phenyl-5-*o-*acetoxybenzylideneoxazolidine*, yellow prisms, m. p. 162·5—163°. G. W. R.

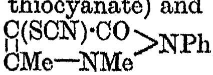
Action of Hydroxylamine and of Hydrazine on the Aryl Monothioamides of Carbethoxyethylmalonate. D. E. Worrall (*J. Amer. Chem. Soc.*, 1923, **45**, 3092—3095; cf. A., 1922, i, 874).—*iso*Oxazoles and pyrazoles were obtained by the action of hydroxylamine and hydrazine, respectively, on carbethoxyethylmalonate monothioamides. Thus carbethoxyethylmalonate monothioanilide gave *ethyl* 3-*anilino*-5-*oxo*-iso*oxazole*-4-*carboxylate*, small needles, m. p. 166°, and the corresponding *pyrazole* ester, fluffy, white needles, m. p. 194—195°. *Ethyl* 3-o-*toluidino*-5-iso-*oxazole*-4-*carboxylate*, flat needles, m. p. 165—167° (decomp.), and the corresponding *pyrazole* ester, white needles, m. p. 215° (decomp.); *ethyl* 3-p-*toluidino*-5-*oxo*iso*oxazole*-4-*carboxylate*, needles and plates, m. p. 172—173° (decomp.), and the corresponding *pyrazole* ester, feathery needles, decomp. above 200°; *ethyl* 3-p-*bromoanilino*-5-*oxo*iso*oxazole*-4-*carboxylate*, slender needles, m. p. 163—170° (decomp.), and the corresponding *pyrazole* ester, needles, m. p. 217°, were obtained. F. B.

4′-Amino-1-phenyl-5-methylbenzthiazole and its Bromination in Glacial Acetic Acid. The Dibromo-product of Gatterman. The Fluorescence of some Benzthiazoles. R. F. Hunter (*Chem. News*, 1923, **127**, 385—386).—An alcoholic solution of dehydrothiotoluidine (4′-amino-1-phenyl-5-methylbenzthiazole) exhibits a green fluorescence in the light of a mercury lamp; its dibromide shows a blue fluorescence in glacial acetic acid solution, and the acetyl derivative is also strongly fluorescent. The dibromide is decomposed by nitrous acid and consequently cannot be diazotised. E. H. R.

Absorption Colours of the Second Order. J. Piccard and F. de Montmollin (*Helv. Chim. Acta*, 1923, **6**, 1011—1019).—It was shown previously that *meri*-quinonoid salts of tetraphenylbenzidine have a yellow colour of the second order (A., 1913, i, 895). It is now shown that Nietzki's rule also applies to such second order colours; the second absorption band can be moved further into the visible spectrum by increasing the molecular weight, changing the colour of the compound from yellow to red. This has been demonstrated by preparing a *meri*-quinonoid salt of diphenyldi-*p*-diphenylylbenzidine, $C_6H_4Ph·NPh·C_6H_4·C_6H_4·NPh·C_6H_4Ph$. *Diphenyl*-p-*diphenylylamine*, $C_6H_4Ph·NPh_2$, is formed by heating diphenylamine with *p*-iododiphenyl in nitrobenzene in presence of potassium carbonate and a little copper; it forms long, nearly colourless crystals, m. p. 114°. It forms a yellowish-green compound with chloranil, and gives a greenish-blue coloration with concentrated sulphuric acid. When oxidised in glacial acetic acid with sodium dichromate, it gives a red colour, changing to green; the green solution is reduced with zinc dust and from the diluted solution *diphenyldidiphenylylbenzidine* can be extracted with chloroform, in 20% yield. It forms a brown powder, m. p. 135—140°. The same substance can be obtained in an impure form by condensing *s*-diphenylbenzidine with *p*-iododiphenyl. All solutions of the compound show a strong violet fluorescence which is excited by ultra-violet light at the limit of the visible spectrum. This benzidine derivative is oxidised by sodium dichromate in glacial acetic acid solution into a *meri*-quinonoid salt which can be precipitated by picric acid as meri-*diphenyldi*-p-*diphenylyldiphenoquinonedi-immonium picrate*, a red powder. Further oxidation gives the green *holo*-quinonoid salt. E. H. R.

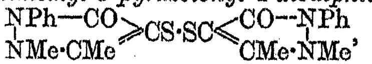
Additive Reactions of Thiocyanogen. H. P. Kaufmann and J. Liepe (*Ber.*, 1923, **56**, [*B*], 2514—2520).—Attempts have been made to estimate enols by titration with solutions of thiocyanogen in the hope of thereby avoiding secondary disturbances such as may be caused by the liberated hydrogen bromide in Meyer's bromine titration method. It is found, however, that the reagent can be applied only under definite conditions; in general applicability and rapidity of execution, the method is not equal to Meyer's process. Quantitative experiments with solutions of thiocyanogen are rendered very difficult on account of the ease with which it becomes polymerised, particularly on exposure to sunlight or to an elevated temperature.

Thiocyanogen reacts with antipyrine in the presence of chloroform to give a mixture of *antipyrine thiocyanate*, colourless, lustrous needles, m. p. 125° (which is also obtained from antipyrine sulphate and potassium thiocyanate) and 4-*thiocyano*-1-*phenyl*-2 : 3-*dimethyl-pyrazol*-5-*one*,



$\begin{matrix}\mathrm{C(SCN){\cdot}CO}\\ \| \\ \mathrm{CMe{-}NMe}\end{matrix}\!\!>\!\mathrm{NPh}$

, colourless crystals, m. p. 147—148°; the constitution of the latter substance follows from its preparation from 4-bromoantipyrine and potassium thiocyanate in boiling aqueous solution. 4-*Thiocyanoantipyrine thiocyanate* has m. p. 84°. 4-Thiocyanoantipyrine is very readily hydrolysed by alkali hydroxide to potassium cyanide, potassium cyanate, and *bis*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolonyl* 4-*disulphide*,



$$\begin{matrix}\mathrm{NPh{-}CO}\\ | \\ \mathrm{NMe{\cdot}CMe}\end{matrix}\!\!>\!\mathrm{CS{\cdot}SC}\!<\!\!\begin{matrix}\mathrm{CO{-}NPh}\\ | \\ \mathrm{CMe{\cdot}NMe}\end{matrix},$$

very pale yellow, hexagonal plates, m. p. 256°; the compound can also be prepared by means of aqueous alcohol. 4-Thiocyanoantipyrine is reduced by zinc and hydrochloric acid in the presence of alcohol to the additive *compound* of zinc chloride and 4-thiolantipyrine, $C_{11}H_{12}ON_2S,ZnCl_2$, a white precipitate from which the thiol could not be isolated.

[With M. Thomas.]—Addition and substitution of free thiocyanogen occur much more slowly than in the case of bromine. Thus ethyl hydrocollidinedicarboxylate reacts with seven atomic proportions of chlorine and four of bromine, but not with iodine; with thiocyanogen, it gives a *di-thiocyano*-derivative, $C_{16}H_{19}O_4N_3S_2$, m. p. 115° (decomp.). *Ethyl collidinedicarboxylate thiocyanate* crystallises in colourless, monoclinic plates, m. p. 133°.

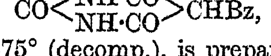
[With M. Thomas.]—Reactions with free cyanogen depend greatly on the solvent used, addition occurring particularly rapidly in the presence of nitromethane (as example of a solvent of high dissociating power). The action of sunlight and of certain catalysts, notably iron, is advantageous. Thus, whereas salicylic acid is indifferent towards thiocyanogen under the usual conditions, it is converted in nitromethane solution in the presence of iron powder into 2-*hydroxy-5-thiocyanobenzoic acid*, monoclinic leaflets, m. p. 167—168°.

H. W.

New Methods of Splitting Pyrimidines. II. Decomposition of Pyrimidines by means of Ferrous Salts. M. H. Pfaltz and O. Baudisch (*J. Amer. Chem. Soc.*, 1923, **45**, 2972—2980; cf. A., 1921, ii, 337).—The splitting of pyrimidines under conditions closely resembling those in the metabolism of plants and animals was accomplished by the action of the system ferrous sulphate–sodium hydrogen carbonate–air and the system sodium pentacyanoaquoferroate–oxygen or air (A., 1900, i, 591) on uracil and thymine. In each case the pyrimidine ring was partly hydrolysed, with the formation of highly coloured intermediate substances which were completely hydrolysed by warm sodium hydrogen carbonate with the production of carbamide. The action was retarded by hydrogenation of the pyrimidine ring as in hydrouracil and by the presence of a methyl group in the 5-position as in thymine, and by the addition of any substance possessing a strong affinity for iron, *e.g.*, ammonia, potassium cyanide. F. B.

5-Benzoylbarbituric Acids. H. Biltz and T. Köhler (*Ber.*, 1923, **56**, [*B*], 2482—2489).—In continuation of the work on 5-acylbarbituric acid (cf. Biltz and Wittek, A., 1921, i, 454), 5-benzoylbarbituric acid has been examined in detail. The position of the benzoyl group is placed beyond doubt by the observed ketonic properties of the compound, by the existence of similar derivatives of 1 : 3-dimethyl- and 1 : 3-diethyl-barbituric acids, and by the inability of alkalis to effect hydrolysis.

5-Benzoylbarbituric acid,



$CO<\substack{NH\cdot CO\\NH\cdot CO}>CHBz$, pale yellow aggregates of prisms, m. p. 275° (decomp.), is prepared by heating barbituric acid with benzoic anhydride at 175° during five hours; it cannot be prepared from barbituric acid, benzoyl chloride, and sodium hydroxide or from barbituric and benzoic acids. The *potassium* salt, rhombic leaflets, decomp. about 315°, is described. It is stable towards sodium hydroxide solution or concentrated hydrochloric acid. It is decomposed by hot fuming nitric acid into alloxan and benzoic or nitrobenzoic acids, and by bromine in aqueous solution at the atmospheric temperature into benzoic and 5 : 5-dibromobarbituric acids. It gives a *hydrazone*, $C_{11}H_{10}O_3N_4$, slender, pale yellow needles, decomp. 260°, and a *phenylhydrazone*, $C_{17}H_{14}O_3N_4$, small, pale yellow needles, decomp. 218°; a semicarbazone could not be obtained. It is decomposed by thiosemicarbazide in boiling aqueous-alcoholic solution into barbituric acid and 2-amino-5-phenylthiodiazole (cf. Young and Eyre, T., 1901, **79**, 57); 5-acetylbarbituric acid yields, in a similar manner, barbituric acid and 5-amino-2-methylthiodiazole. The action of hydroxylamine on 5-benzoylbarbituric acid in boiling alcoholic solution gives a *substance*, colourless, lustrous, hexagonal platelets, m. p. 261°, which is regarded as the oxime of 5-amino-5-benzoylbarbituric acid, $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C(NH_2)\cdot CPh:N\cdot OH$; it is converted by hot, concentrated nitric acid into alloxan, by highly concentrated hydriodic acid into benzoylbarbituric acid, and by bromine water into alloxan and benzaldehyde. 5-Benzoylbarbituric acid is converted by sodium hydroxide and methyl sulphate into the *methyl ether* of the enolic form of 5-benzoylbarbituric acid, $CO<\begin{matrix}NH\text{——}CO\\NH\cdot C(OMe)\end{matrix}\geqslant CBz$, colourless, lustrous prisms, decomp. 105°; the corresponding *phenylhydrazone*, $C_{18}H_{16}O_3N_4$, decomp. 225°, is described. The ethylation of 5-benzoylbarbituric acid could not be effected by ethyl sulphate or ethyl bromide, magnesium oxide, and carbon tetrachloride at 140°.

1-Methylbarbituric acid and benzoic anhydride react at 130—140° to give 5-*benzoyl*-1-*methylbarbituric acid*, small, pale brown prisms, decomp. 225° (*phenylhydrazone*, slender, yellow needles, decomp. 205°). 5-*Benzoyl*-1-*ethylbarbituric acid*, flattened prisms, m. p. 205° (decomp.), and its *phenylhydrazone*, slender needles, decomp. 190° after darkening at 175°, are described. 1 : 3-Dimethylbarbituric acid reacts with benzoic anhydride at 130°, but the expected 5-benzoyl-1 : 3-dimethylbarbituric acid could not be isolated from the product of the reaction in the homogeneous condition; it is characterised as the *phenylhydrazone*, $C_{19}H_{18}O_3N_4$, colourless, quadratic leaflets, decomp. 218°. 5-Benzoyl-1 : 3-diethylbarbituric acid could not be caused to crystallise; the *phenylhydrazone*, $C_{21}H_{22}O_3N_4$, forms long, yellow leaflets, decomp. 164°.

Attempts to cause interaction between barbituric acid and oxalic acid, oxalyl chloride, oxalyl bromide, or phthalic anhydride were not successful. Thiobarbituric acid does not react smoothly with acetic or benzoic anhydrides. The acetyl group of 5-acetylbarbituric acids does not appear to be capable of condensing with aldehydes. H. W.

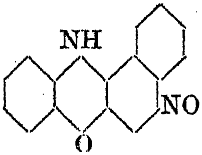
Alkyl*iso*propylbarbituric Acids. F. HOFFMANN LA ROCHE & Co. (Austr. Pat. 92386; from *Chem. Zentr.*, 1923, iv, 665).—In modification of an earlier patent (A., 1922, i, 872) other alkyl halides are used in place of allyl bromide. 5-*Methyl*-5-*isopropylbarbituric acid*, from *iso*propylbarbituric acid and methyl iodide, forms crystals, m. p. 186—187°. 5 : 5-*Diisopropylbarbituric acid* forms crystals, m. p. above 230° (decomp.). G. W. R.

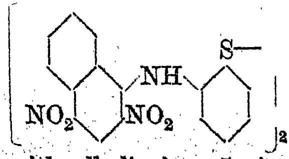
Preparation of New Barbituric Acid Compounds. CHEMISCHE FABRIK AUF AKTIEN, VORM. E. SCHERING (Brit. Pat. 198379; addn. to 158558; cf. A., 1922, i, 582).—New compounds, similar in properties to that previously described (*loc. cit.*) are obtained by replacing the diethylbarbituric acid in the original process by dipropyl-, diallyl-, or phenylethyl-barbituric acid. The products of these three fusions melt respectively at 82—86°, 85—88°, and 106—120°. W. T. K. B.

Diketopiperazine Derivatives. P. Karrer, C. Gränacher, and A. Schlosser (*Helv. Chim. Acta*, 1923, **6**, 1108—1112).—Benzyl chloride reacts with the silver salt of glycine anhydride to give 2 : 5-*dihydroxydihydropyrazine dibenzyl ether*, crystallising in white leaflets, m. p. 164°. The reaction therefore follows a different course from that of methyl iodide on the anhydride (A., 1922, i, 235). The new compound is readily hydrolysed by boiling dilute acids to benzyl alcohol and glycine, and in this respect differs markedly from its isomerides, *N* : *N'*-dibenzylglycine anhydride and diketo-2 : 5-dibenzylpiperazine. E. H. R.

New Syntheses in the Quinoneimide Dye Group. I. Syntheses with 1-Chloro-2 : 4-dinitronaphthalene. F. Kehrmann (with A. van Baerle) (*Ber.*, 1923, **56**, [*B*], 2385—2390).—A number of known and some new quinoneimide dyes have been prepared by condensing 1-chloro-2 : 4-dinitronaphthalene with different bases. In many cases the toluene-*p*-sulphonic ester of Martius's yellow (2 : 4-dinitro-α-naphthol) can also be used.

o-2 : 4-*Dinitronaphthylaminodiphenylamine* is obtained by condensing the dinitrochloronaphthalene with *o*-aminodiphenylamine in alcohol; it forms large, brownish-red prisms containing benzene from that solvent, which lose benzene and turn black at 70°, m. p. 140°. With 5-chloro-2-aminodiphenylamine, the corresponding 5-*chloro*-2-(2 : 4-*dinitronaphthylamino*)*diphenylamine* is obtained, dark brown leaves, m. p. 110°. Both these compounds are reduced smoothly by stannous chloride to rosinduline and chlororosinduline respectively. The rosindones are obtained by fusing the dinitro-compound with benzoic acid.

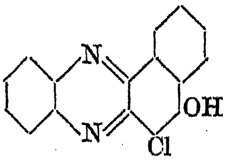




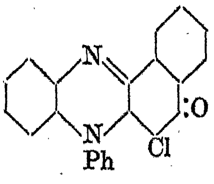
By condensing 2 : 4-dinitro-1-naphthyltoluenesulphonate with *o*-aminophenol, *o*-2 : 4-dinitronaphthylaminophenol is obtained which, by careful treatment with aqueous sodium hydroxide is converted into 5-*nitro*-7 : 12-*naphthaphenoxazine* (annexed formula), a violet precipitate which decomposes when heated. An acetyl derivative could not be obtained, but instead the known phenonaphthoxazone was formed. With *oo'*-diaminodiphenyl disulphide the above toluenesulphonate condenses to give o-*bis*-2 : 4-*dinitronaphthylaminophenyl disulphide* (annexed formula), orange-yellow leaflets, m. p. 169°. With *o*-aminothiophenol it gives o-2 : 4-*dinitronaphthylaminophenyl mercaptan*, a lemon-yellow, crystalline powder, m. p. 198°, which by careful treatment with alkali gives 5-*nitro*-7 : 12-*naphthaphenthiazine*, nearly black needles with a brassy reflex, m. p. 156° (decomp). It is much more stable than the corresponding oxazine. A by-product of the last condensation, yellow, glistening crystals, m. p. 150°, appeared to be 2 : 4-*dinitronaphthyl*-o-*aminophenyl sulphide*.

E. H. R.

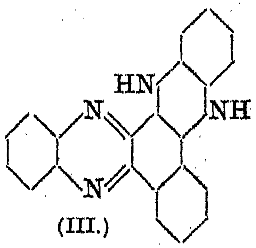
New Syntheses in the Quinoneimide Dye Group. II. Steric Influence in the Condensation of Hydroxyquinones with *o*-Diamines. F. Kehrmann [with C. Buffat] (*Ber.*, 1923, 56, [*B*], 2390—2394).—It has long been known that substituted quinones such as chloranilic acid and 3-chloro-4-hydroxy-1 : 2-naphthaquinone react with difficulty or not at all with *o*-diamines, but it is now found that these reactions proceed under suitable conditions. Thus when chloranilic acid is heated with *o*-phenylenediamine hydrochloride and a large quantity of benzoic acid at the boiling point, 1 : 4-*dichloro*-2 : 3-*dihydroxyphenazine* is formed, dark brownish-red, metallic crystals, blackening at 310°. It gives a dichroic sulphuric acid solution, brown in thick, greenish-yellow in thin layers. With *o*-aminodiphenylamine, chloranilic acid gives 1 : 4-*dichloro-2-hydroxy*apo*safranone*, dark, reddish-brown crystals with a weak, brassy lustre, decomposing at 285°. 3-Chloro-4-hydroxy-1 : 2-naphthaquinone with *o*-phenylenediamine gives 6-*chloro*-5-*hydroxy*-αβ-*naphthaphenazine* (formula I), dark red, brassy crystals decomposing at about 280°. It gives a dirty yellowish-green colour with concentrated sulphuric acid, ponceau-red with hot alkali. With *o*-aminodiphenylamine, 3-chloro-2-hydroxy-1:4-naphthaquinone gives 6-*chlororosindone* (formula II), red needles with golden lustre, m. p. 255°, giving a dark yellowish-green colour in sulphuric acid. With 2-amino-5-chlorodiphenylamine, 6 : 9-*dichlororosindone* is formed, red needles with strong gold reflex, m. p. 242—243°, giving a dirty violet-red colour in sulphuric acid.



(I.)



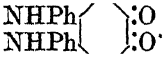
(II.)

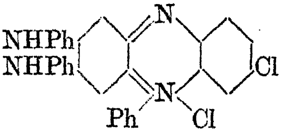


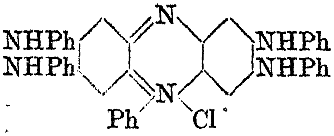
(III.)

When the above 5-hydroxy-6-chloronaphthaphenazine is fused with *o*-phenylenediamine, a new *dihydronaphthadiphenazine* (formula III) is formed, golden-yellow leaflets with brassy reflex, m. p. 263°. Its *hydrochloride* forms dark red, metallic needles, and it gives a pure green colour in concentrated sulphuric acid.

E. H. R.

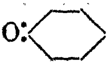
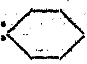
New Syntheses in the Quinoneimide Dye Group. III. Syntheses of Induline-3*B* and -6*B*. F. Kehrmann [with W. Klopfenstein] (*Ber.*, 1923, 56, [*B*], 2394—2397).—The constitutional formulæ assigned to Induline-3*B* and -6*B* have now been confirmed by synthesis of these dyes from dianilino-*o*-quinone,  When this is condensed with 2-amino-5-chlorodiphenylamine hydrochloride in alcohol, 3-*chloro*-8-*anilinophenyl*aposafranine (annexed formula) is formed, crystallising in needles with a green reflex. The free *base* forms brownish-red needles, m. p. 258°. The colour in concentrated sulphuric acid is violet-blue, becoming violet and then Bordeaux-red on dilution. When this is boiled with aniline and aniline hydrochloride, the ring chlorine is replaced by the anilino-group, forming 8-*anilino*-3 : 7-*diphenylphenosafranine*, identical with Induline-3*B*. The free base forms nearly black leaflets with a weak green reflex, m. p. 242°. Induline-3*B* is converted into Induline-6*B*, 2 : 8-dianilino-3 : 7-diphenylphenosafranine (annexed formula), by boiling with aniline and aniline hydrochloride in presence of 1 mol. of mercuric oxide. The free base forms greenish-black metallic crystals, m. p. 286—288°; the *hydrochloride* and *hydrobromide* both form crystals with a coppery lustre, insoluble in water.

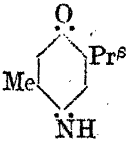




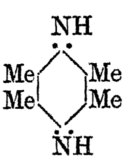
E. H. R.

New Syntheses in the Quinoneimide Dye Group. IV. The Colour of the Simple Quinoneimines. F. Kehrmann [with B. Cordone] (*Ber.*, 1923, 56, [*B*], 2398—2405).

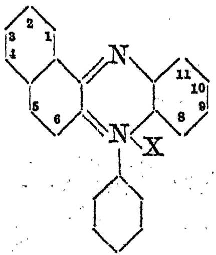
—In a previous paper (A., 1922, ii, 333), the rule was established that the effect of salt formation on the colour of basic nitrogen compounds is to intensify the colour if the unsaturated condition persists. This rule has now been found to apply to compounds of the quinoneimine series, of which several new members have been prepared. *Thymoquinonemonoimine* (annexed formula) was prepared by oxidising *p*-aminothymol with silver oxide in ethereal solution; it crystallises in bright yellow, silky leaflets, m. p. 74—75°. It is stable for some time in the dark at low temperatures and is much less sensitive to light than *p*-benzoquinonemonoimine. Its salts are deeper yellow in colour than the compound itself; the *hydrochloride* is obtained as a voluminous, yellow precipitate from ether; the *picrate*, which is stable for some time in water, forms bright yellow, sparingly soluble crystals. The monoimines of benzo- and tolu-quinone were prepared afresh to confirm their yellow colour. Benzoquinonechloroimine, O::NCl, is also yellow, but benzoquinonedi-imine is colourless, whilst its dihydrochloride is yellow. Benzoquinonedichlorodi-imine, ClN::NCl, is colourless; it



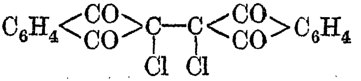
gives a salt only with concentrated sulphuric acid, and this is yellow. *Duroquinonedi-imine* (annexed formula) was obtained by oxidising diaminodurene with silver oxide in ether; it forms colourless crystals, not very sensitive to light, m. p. 134—135°. It dissolves in dilute mineral acids, giving bright yellow solutions which soon decompose with deposition of duroquinone. The salts, which can be obtained in crystalline form from ether, are bright yellow. The results show that the carbonyl group is a stronger chromophore than the iminocarbonyl group $\cdot C{:}NH$. This is also shown by the fact that whilst tetramethyldiaminobenzophenone is yellow, auramine base is colourless. E. H. R.



Determination of the Constitutional Formulæ of Colouring Matters from their Absorption Spectra. V. F. Kehrmann and M. Sandoz (*Helv. Chim. Acta*, 1923, **6**, 982—994).—The absorption spectra of the mono-acid and di-acid salts of phenyl-αβ-benzophenazonium (annexed formula) and of the mono-, di-, and tri-acid salts of nine of its monoamino-derivatives have been measured. The mono-salt of the parent substance is yellow with orange fluorescence, the di-salt violet; both have an ortho-quinonoid structure. The amino derivatives, 1-, 2-, 3-, and 4- form a group. Their mono-salts are bluish-green, except that of the 3-amino-derivative, which is brown; their di-salts are yellow, similar to the mono-salt of the parent substance, and their tri-salts deep red, comparable with the di-salt of the parent. The 1-amino-compound does not form a tri-salt, probably on account of steric hindrance. All these salts are given an ortho-quinonoid structure. The mono-salt of the 10-amino-derivative (violet) is probably also ortho-quinonoid. The 9- and 5-amino-compounds form another group; they behave similarly to *apo*safranine (A., 1920, ii, 142). The mono-acid salt (scarlet) and the di-acid salt (green) are para-quinonoid, whilst the tri-acid salt (violet) has the ortho-quinonoid structure. The fact that the di-acid salts can be diazotised indicates that the solutions contain a small amount of the yellow, ortho-quinonoid di-acid salt in equilibrium with the para-quinonoid form. Two amino-derivatives, the meta- and para-, were prepared having the amino-group in the external benzene ring. Here the auxochromic effect of the amino-group is reduced to a minimum, and there is little difference between the colours of the mono-acid salt and of the di-acid salt, both being yellow in solution; the tri-acid salt is violet, and all three are ortho-quinonoid. Curves are given showing the absorption spectra of all the salts examined. E. H. R.



Spirans. XII. Heterocyclic Dispirans and the Nature of the Basic Properties of the Imino-group. D. Radulescu (*Bul. Soc. Ştiinţe Cluj*, 1922, **1**, 356—360; from *Chem. Zentr.*, 1923, iii, 1081; cf. this vol., i, 58).—Heterocyclic dispirans have been prepared by the author by the action of *o*-diamines on dichlorobisdiketohydrindene (I). *Piperazinebis*-3-1 : 3-*diketohydrindene*-2 : 2 : 3 : 2-*dispiran*, $C_{20}H_{14}O_4N_2$, (II) forms yellow prisms, m. p. 249° (corr.). The *spiran* (III), $C_{24}H_{14}O_4N_2$, forms microcrystalline brown prisms, m. p. 272° (corr.). Spiran III is scarcely basic, whilst the dispiran II is moderately basic. This is explained by Thiele's theory of partial valencies, which is also applicable to the slight basicity of pyrrole and indole. Spirans with tertiary nitrogen are more basic. N : N′-*Dipiperidylbis*-1 : 3-*diketohydrindene* (IV) forms orange prisms, m. p. 174°. The *diethylamino*-derivative of the latter forms yellow prisms, m. p. 129°, and the *dibenzylamino*-derivative yellow needles, m. p. 178°. The author concludes that the hydroxy-derivatives corresponding with the amines must be strongly acid. The compound described by Gabriel and Leupold (A., 1898, i, 481) as bisdiketohydrindene oxide (V) is really a spiran pinacone (VI). It is hydrolysed by weak acids and alkalis to diketohydrindene, and its decomposition products, and phthalonic acid.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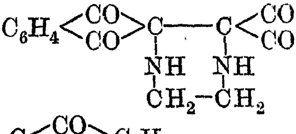
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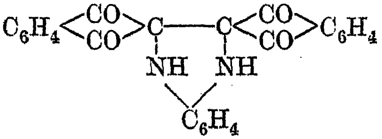
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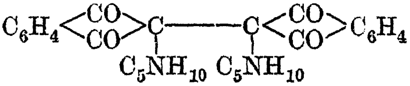
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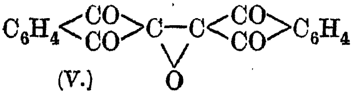
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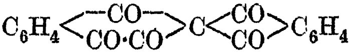
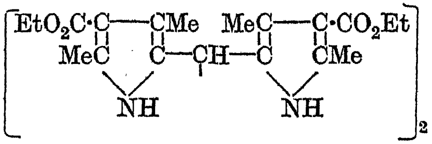

(VI.)

G. W. R.

Reactions of certain Substituted Guanidines with Sulphur. G. Bruni and T. G. Levi (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 313—316).—When heated together in a sealed tube at 260—270°, *s*-diphenylguanidine and sulphur give a good yield of mercaptobenzthiazole. In aniline solution, subjected to prolonged boiling in a reflux apparatus, the reaction gives rise to little or no mercaptobenzthiazole, but to anilinobenzthiazole (cf. Hofmann, A., 1880, 388; Jacobson and Frankenbacher, A., 1891, 1048; Hugershoff, A., 1903, i, 865; and Rassow and Döhle, A., 1916, i, 747): $NHPh{\cdot}C(:NH){\cdot}NHPh+S=C_6H_4{<}\overset{N}{\underset{S}{}}{>}C{\cdot}NHPh+NH_3$; the *acetyl* derivative of anilinobenzthiazole has m. p. 162—163°.

Mercaptobenzthiazole is formed in good yield when phenylguanidine, and in poor yield when *s*-triphenylguanidine, is heated in a sealed tube with sulphur at 270° (cf. Sebrell and Bord, this vol., i, 89). T. H. P.

Tetrapyrrlethanes. I. HANS FISCHER and M. SCHUBERT (*Ber.*, 1923, **56**, [*B*], 2379—2384; cf. A., 1923, i, 707).—Glyoxal can be condensed with ethyl 2 : 4-dimethylpyrrole-3-carboxylate in alkaline or, better, in acid alcoholic solution, to form *tetra*(*3-carbethoxy-2 : 4-dimethyl-5-pyrryl*)*ethane* (annexed formula), which crystallises in colourless leaflets, m. p. 282°. It gives an intense green solution in acetic acid. Oxidation with ferric chloride gives 2 mols. of bis-2 : 4-dimethyl-3-carbethoxypyrrylmethene, whilst reduction with hydriodic acid in acetic acid solution gives a mixture of pyrroles containing 2 : 4-dimethyl- and 2 : 4 : 5-trimethyl-pyrrole. Potassium methoxide converts the ethane compound into tetramethylpyrrole. It can also be hydrolysed to *tetra*(*3-carboxy-2 : 4-dimethylpyrryl*)*ethane*, small tetrahedral crystals, m. p. 233° (decomp.), but this product is not identical with that obtained by condensing glyoxal with 2 : 4-dimethylpyrrole-3-carboxylic acid.



The relationship of tetrapyrrylethane derivatives with blood- and bile-pigments is discussed, the conclusion being that there is a closer relationship with the latter. This conclusion is supported by spectroscopic examination of copper and zinc salts of a number of dipyrrylmethene derivatives. E. H. R.

Diallylxanthine. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 97978; from *Chem. Zentr.*, 1923, iv, 830).—By heating 4 : 5-*diamino*-2 : 6-*dioxo*-1 : 3-*diallylpyrimidine*, obtained by condensation of diallylcarbamide with cyanoacetic acid or ethyl cyanoacetate, treatment with nitrous acid, and reduction with formic acid, 5-*formylamino*-4-*amino*-2 : 6-*dioxo*-1 : 3-*diallylpyrimidine* is obtained. This is heated with *N* sodium hydroxide solution at 100° and then acidified, whereby 1 : 3-*diallylxanthine*, m. p. 155—156°, is obtained. The intermediate compound, 4-*amino*-6-*oxo*-5-*oximino*-1 : 3-*diallylpyrimidine*, can also be obtained by direct condensation of *s*-diallylcarbamide with ethyl oximinocyanoacetate. G. W. R.

1 : 3 : 7-Triallylxanthine. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 97979; from *Chem. Zentr.*, 1923, iv, 830; cf. preceding abstract).—1 : 3-*Diallylxanthine* is alkylated, for example by treatment with allyl benzoate in the presence of ethyl-alcoholic potassium hydroxide at 80°. 1 : 3 : 7-*Triallylxanthine* has m. p. 57—58°; b. p. 176°/5 mm. G. W. R.

Oxidation of Uric Acid with Ferrous Salts. I. M. H. PFALTZ (*J. Amer. Chem. Soc.*, 1923, **45**, 2980—2984; cf. this vol., i, 210).—Cleavage of the uric acid molecule was accomplished by the systems ferrous sulphate–sodium hydrogen carbonate–air and sodium pentacyanoaquoferroate–air or oxygen, but not by the system ferrous sulphate–oxygen. The action was similar to that which occurred with pyrimidines. F. B.

Action of Alkali on Substituted Uric Acids. I. 9-Phenyl-1 : 3-dimethyluric Acid. E. S. GATEWOOD (*J. Amer. Chem. Soc.*, 1923, **45**, 3056—3064; cf. A., 1923, i, 253).—This substituted uric acid was decomposed instantaneously at 100° with 4*N* sodium hydroxide with the elimination of methylamine. On acidifying the solution, carbon dioxide was evolved, and crystals, m. p. 249—250°, of 3-*phenyl*iso*hydantoin-5-carboxyl*-o-*methylamide* separated. This was further decomposed by alkali into phenylcarbamide, methylamine, oxalic acid, and formic acid, whilst oxidation with hydrogen peroxide in alkaline solution yielded *5-hydroxy-3-phenylhydantoin 5-carboxyl*-o-*methylamide*, large, thin, rectangular plates, m. p. 195—196°. This was further decomposed by alkali into methylamine, phenylcarbamide, and meso-oxalic acid. 9-*Phenyl*-1 : 7-*dimethyluric acid* was synthesised. It did not melt below 280° and was not affected by boiling with 4*N* sodium hydroxide for ten minutes. F. B.

The Activation of Halogen and Methyl in Aromatic Compounds by the Azo-group, ·N:NR. W. BORSCHE and I. EXSS (*Ber.*, 1923, **56**, [*B*], 2353—2357).—Experiments with 4-chloro-3-nitroazobenzene and 6-chloro-3-nitro-4′-methoxyazobenzene, show that the azo-group in ortho- or para-position to the halogen imparts to it increased activity. These compounds react more readily with hydrazine, ammonia, aniline, or sodium ethoxide than *o*- or *p*-chloronitrobenzene, although not so readily as chloro-2 : 4-dinitrobenzene. On the other hand, benzeneazo-2-nitro-*p*-toluene does not react with benzaldehyde to form a stilbene derivative as does 2 : 4-dinitrotoluene.

4-Chloro-3-nitroazobenzene, from 4-chloro-3-nitroaniline and nitrosobenzene, forms brown needles, m. p. 84°. *6-Chloro-3-nitro-4′-hydroxyazobenzene*, from diazotised 6-chloro-3-nitroaniline and phenol, forms red needles, m. p. 218°; it is methylated by methyl sulphate to *6-chloro-3-nitro-4′-methoxyazobenzene*, deep yellow leaflets, m. p. 103°. *Benzeneazo-2-nitro*-p-*toluene*, from 2-nitro-*p*-toluidine and nitrosobenzene, forms brown needles, m. p. 106°.

3-Nitro-4-hydrazinoazobenzene, $Ph{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}NH{\cdot}NH_2$, forms red needles, m. p. 206° (decomp.); with acetophenone it forms the corresponding *hydrazone*, $Ph{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}NH{\cdot}N{:}CMePh$, red needles, m. p. 195°. *2-Nitro-4-benzeneazo-4′-hydroxyazobenzene*, $Ph{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}N_2{\cdot}C_6H_4{\cdot}OH$, obtained from the above hydrazine and *p*-benzoquinone, forms brown needles, m. p. 203° (decomp.); with quinoneoxime, the hydrazine forms an *oximehydrazone*, $Ph{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}NH{\cdot}N{:}C_6H_4{:}N{\cdot}OH$, a red, crystalline powder, m. p. 235° (decomp.).

3-Nitro-4-aminoazobenzene forms red needles, m. p. 173·5°. *3-Nitro-4-piperidinoazobenzene*, by condensing 4-chloro-3-nitroazobenzene with piperidine, forms orange-red tablets, m. p. 64°. *3-Nitro-4-anilinoazobenzene*, $Ph{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}NHPh$, forms brown needles,

m. p. 124°. 3-*Nitro-4-methoxyazobenzene* crystallises in orange-red needles, m. p. 107°.

3-*Nitro-4'-methoxy-6-hydrazinoazobenzene* forms red needles, m. p. 173°; with *p*-anisaldehyde it gives the corresponding *hydrazone*, red needles, m. p. 208°. 5-*Nitro-2-amino-4'-methoxyazobenzene* forms brownish-yellow needles, m. p. 136°. 3-*Nitro-6 : 4'-dimethoxyazobenzene* forms orange-yellow needles, m. p. 123°. E. H. R.

Thiophenols. V. Salts and Additive Compounds of *oo'*-Azophenyl Methyl Sulphide and *oo'*-Azoxyphenyl Methyl Sulphide. K. BRAND and P. GROBEL (*Ber.*, 1923, **56**, [*B*], 2563—2567).—An extension of the work of Brand and Wirsing (A., 1912, i, 666; 1913, i, 406) on the para-compounds to the ortho-series.

The following salts of *oo'*-dimethylthiolazobenzene,

$$SMe\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot SMe,$$

are described: the *perchlorate*, $C_{14}H_{14}N_2S_2,HClO_4$, bluish-violet needles which are very sensitive to moisture, m. p. 154°; the *sulphate*, $C_{14}H_{14}N_2S_2,2H_2SO_4$, dark violet needles; the very unstable *hydrochloride*, blue needles, and its additive *compounds* with stannic chloride, $C_{14}H_{14}N_2S_2,HCl,SnCl_4$, blackish-violet needles, with ferric chloride, $C_{14}H_{14}N_2S_2,HCl,FeCl_3$, dark violet, almost black needles, and mercuric chloride, an unstable, blue compound.

oo'-Dimethylthiolazobenzene is transformed by methyl sulphate into the *methosulphate*, $N_2(C_6H_4\cdot SMe_2\cdot O\cdot SO_2\cdot OMe)_2$, coarse crystals, m. p. 189° (decomp.), which is converted into the corresponding *iodide*, $C_{14}H_{14}N_2S_2,2MeI$, long, red needles, m. p. 154°, which readily loses methyl iodide when preserved, the *bromide*,

$$C_{14}H_{14}N_2S_2,2MeBr,$$

m. p. 154°, and the unstable *thiocyanate*, decomp. 102—105°.

o-Nitrophenyl methyl sulphide is reduced by sodium and methyl alcohol to *oo'-dimethylthiolazoxybenzene*, crystals, m. p. 72°, from which the corresponding *methosulphate*, $C_{14}H_{14}ON_2S_2,2Me_2SO_4$, yellow leaflets, m. p. (indefinite) 167—169° (decomp.) after becoming red at 160—162°, and the *methiodide*, $C_{14}H_{14}ON_2S_2,2MeI$, m. p. 103° (decomp.), are obtained.

oo'-Dimethylthiolazobenzene and the azoxy-compound combine with iodine in chloroform solution to give the *compounds*,

$$C_{14}H_{14}N_2S_2,2I_2,$$

m. p. 155° after evolving iodine at 140°, and $C_{14}H_{14}ON_2S_2,2I_2$, dark green needles, m. p. 113—114°; the corresponding sulphonium methosulphates when treated in aqueous solution with iodine and potassium iodide yield the *compounds* $C_{14}H_{14}N_2S_2,2MeI,2I_2$, m. p. 113—115° (decomp.), and $C_{14}H_{14}ON_2S_2,2MeI,2I_2$, m. p. 103° (decomp.) after darkening at 100°.

The following additive compounds are described: the *substance*, $C_{14}H_{14}N_2S_2,AgNO_3$, from the components in boiling aqueous-alcoholic solution, orange-coloured needles, which is completely decomposed into its components by hot water; the *salt*,

$$C_{14}H_{14}ON_2S_2,AgNO_3,$$

yellow needles; oo'-*diethylthiolazobenzene silver nitrate*,

$$C_{16}H_{18}N_2S_2,AgNO_3,$$

orange-coloured leaflets; *o-nitrophenyl methyl sulphide silver nitrate*, $NO_2\cdot C_6H_4\cdot SMe,AgNO_3$, yellow leaflets, m. p. 122°. H. W.

The Influence of Sulphonic Groups on the Colour of Azo-dyes. W. Meuly (*Helv. Chim. Acta*, 1923, **6**, 931—935).—To determine the influence of the number and position of sulphonic groups on the colour of azo-dyes, spectroscopic comparison was made of a large number of secondary bisazo-dyes, in which the first component was an aniline mono- or di-sulphonic or a naphthylamine mono-, di-, or tri-sulphonic acid, the middle component was cresidine (3-amino-*p*-cresol ether) and the end component an α- or β-naphthol mono-, di-, or tri-sulphonic acid. In every case, an additional sulphonic group, in either the first or the end component, deepens the colour, but the effect diminishes as the number of sulphonic groups increases. In the naphtholsulphonic acids, the effect of changing the position of the sulphonic group is smaller than the effect of an additional group. Similar results were obtained with a number of monoazo- and trisazo-dyes. As an example of the effect of additional sulphonic groups, the dye from sulphanilic acid, 3-amino-*p*-cresol ether and 1 : 4-naphtholsulphonic acid is red, whilst the corresponding dye using 1 : 3 : 6 : 8-naphtholtrisulphonic acid is violet. An absorption band may be shifted 10 to 20 μμ by a single sulphonic group, the influence being generally greater in the end component than in the first component. These results apply both to aqueous and to alcoholic solutions; in sulphuric acid and formic acid solutions the absorption bands are shifted in the opposite direction by sulphonic groups. [Cf. *B.*, 86.]

E. H. R.

Certain Double Salts of Diazo-compounds with Lead Tetrachloride. E. Sakellarios (*Ber.*, 1923, **56**, [*B*], 2536—2541).—A series of double salts of the general formula $(ArN_2Cl)_2PbCl_4$ has been prepared. They are generally yellow in colour and insoluble in water. They are decomposed when heated with water with production of phenols. Thermal decomposition in the presence of inert solvents, such as carbon tetrachloride or benzene, gives *p*-chloronitrobenzene from the *p*-nitrodiazonium compound and mixtures of chlorinated benzenes from the benzenediazonium salt. The *p*-tolyl-, *m*-nitrophenyl-, and *p*-chlorophenyl-diazonium compounds are remarkably stable towards heat. The double salts dissolve in concentrated sulphuric acid with separation of lead tetrachloride and production of the diazonium sulphate. They couple immediately with an alkaline solution of β-naphthol and retain this power after being preserved during many months in a desiccator; an exception is, however, provided by the benzenediazonium salt which undergoes rapid decomposition. Direct sunlight and increased temperature facilitate the decomposition in a remarkable degree.

The lead tetrachloride solution is prepared by dissolving lead carbonate in concentrated hydrochloric acid and passing chlorine into the mixture at 10° until the suspended lead chloride is dissolved; excess of chlorine is removed in a current of air. The solution thus prepared is added to the requisite diazonium solution at −5° when the double salts separate. The following individual substances are described: the salt $(PhN_2Cl)_2PbCl_4$, straw-yellow leaflets, and the similarly constituted *compounds* from *p*-toluidine (a yellow, crystalline powder), *p*-chloroaniline (yellow leaflets), *p*-nitroaniline (yellow leaflets), and *m*-nitroaniline.

Ethylamine hydrochloride and lead tetrachloride give the *compound* $(EtNH_2\cdot HCl)_2PbCl_4$, yellow leaflets, which is decomposed by water with formation of ethyldichloroamine, b. p. 89°. H. W.

Characterisation of Aminoazo-derivatives. G. CHARRIER and A. BERETTA (*Gazzetta*, 1923, **53**, 729—760).—The authors find that the reaction suggested by Nietzki and Ernst (A., 1890, 1114) for characterising the primary aromatic amino-group (cf. Reitzenstein, A., 1903, i, 815; Meigen, A., 1908, i, 580; Küchel, *Diss. Giessen*, 1909) and based on the action of 1-chloro-2 : 4-dinitrobenzene in alcoholic solution and in presence of sodium acetate, followed by reduction of the resulting 2 : 4-dinitrodiarylamino-derivative to nitroaminodiarylamino-compound by means of sodium sulphide, is general for all aminoazo-derivatives irrespective of the position of the amino-group to the azo-group. The yield of the condensation product is moderately good from the *p*- and *m*-aminoazo-compounds, but less from the ortho-compounds, especially those of the naphthalene series. However, no resin is formed and the product is usually almost insoluble in alcohol, so that purification is easy.

[With A. NANI, L. ALBANI, A. DE LEONIBUS, G. DRISALDI, P. PAVESI, and O. TAVAZZANI.]—*2′-Benzeneazo-2 : 4-dinitrodiphenylamine*, $NPh{:}N\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)_2$, obtained by the action of 1-chloro-2 : 4-dinitrobenzene on *o*-aminoazobenzene, forms slender, orange-yellow needles, m. p. 206°, dissolves in concentrated sulphuric acid with a green coloration, and resists boiling acetic anhydride. When suspended in alcohol and treated with sodium sulphide, it yields *2′-benzeneazo-4-nitro-2-aminodiphenylamine*,

$$NPh{:}N\cdot C_6H_4\cdot NH\cdot C_6H_3(NH_2)\cdot NO_2,$$

which crystallises in slender, deep red needles, m. p. 151°, and gives a *benzoyl* derivative, $C_{25}H_{19}O_3N_5$, crystallising in slender, yellow needles, m. p. 199°.

*2′-*p*-Tolueneazo-2 : 4-dinitro-4′-methyldiphenylamine*,

$$C_6H_4Me\cdot N{:}N\cdot C_6H_3Me\cdot NH\cdot C_6H_3(NO_2)_2,$$

prepared from *o*-tolueneazo-*p*-toluidine, forms lustrous, red needles, m. p. 232°, gives a green solution in concentrated sulphuric acid, and on reduction with sodium sulphide yields *2′-*p*-tolueneazo-4-nitro-2-amino-4′-methyldiphenylamine*,

$$C_6H_4Me\cdot N{:}N\cdot C_6H_3Me\cdot NH\cdot C_6H_3(NH_2)\cdot NO_2,$$

which crystallises in reddish-brown needles, m. p. 166°, and gives a *benzoyl* compound, $C_{27}H_{23}O_3N_5$, separating in yellow needles, m. p. 206°.

m-Aminoazobenzene may be obtained in satisfactory yield by benzoylating *m*-nitroaniline, reducing the *m*-nitrobenzanilide to *m*-aminobenzanilide, and converting the latter, by means of nitrosobenzene, into the benzoyl derivative of *m*-aminoazobenzene. The melting point of *m*-aminoazobenzene, given by Mills (T., 1895, 67, 917) as 56—57°, is found to be 62°.

3′-*Benzeneazo*-2 : 4-*dinitrodiphenylamine*,

$$NPh{:}N\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)_2,$$

prepared from *m*-aminoazobenzene, crystallises in orange-yellow leaflets, m. p. 162°, and dissolves in concentrated sulphuric acid, giving a red coloration.

4′-Benzeneazo-2:4-dinitrodiphenylamine, prepared from *p*-aminoazobenzene, has m. p. 176° (cf. Walther and Lehmann, A., 1904, i, 352). 4′-*Benzeneazo*-4-*nitro*-2-*aminodiphenylamine*, $C_{18}H_{15}O_2N_5$, obtained by reducing the preceding compound, forms minute, deep red crystals, m. p. 164°; its *acetyl* compound crystallises in slender, yellow needles, m. p. 153°, and its *benzoyl* derivative in yellow needles, m. p. 226°.

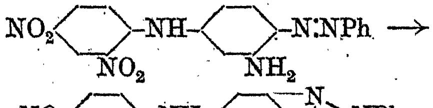
4′-o-*Tolueneazo*-2 : 4-*dinitro*-2′-*methyldiphenylamine*,

$$C_6H_4Me\cdot N{:}N\cdot C_6H_3Me\cdot NH\cdot C_6H_3(NO_2)_2,$$

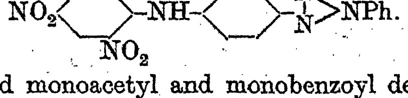
prepared from *o*-tolueneazo-*o*-toluidine, forms deep red needles, m. p. 186°, dissolves in concentrated sulphuric acid to a reddish-violet solution, and, on reduction with sodium sulphide and alcohol, yields 4′-o-*tolueneazo*-4-*nitro*-2-*amino*-2′-*methyldiphenylamine*, which separates in reddish-brown needles, m. p. 159°. 4′-p-*Tolueneazo*-2 : 4-*dinitro*-2′-*methyldiphenylamine*, prepared from *p*-tolueneazo-*o*-toluidine, crystallises in slender, lustrous, red needles, m. p. 151°, and dissolves in concentrated sulphuric acid, giving a violet-red coloration.

The action of 1-chloro-2 : 4-dinitrobenzene on *m*-diaminoazobenzenes results in the replacement by 2 : 4-dinitrophenyl of a hydrogen atom of the amino-group situate in the para-position to the azo-group. The amino-group in the ortho-position to the azo-group does not enter into the reaction, even when the chlorodinitrobenzene is taken in large excess; this appears to be due to the fact that the mono-condensation product is insoluble in alcohol and is hence removed from the sphere of reaction. The resulting diphenylamine derivatives have constitutions analogous to (I) and on oxidation yield the corresponding triazole compounds (II):

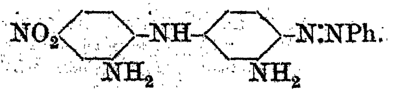
(I.)



(II.)



They readily yield monoacetyl and monobenzoyl derivatives, the substituent groups entering the amino-group in the ortho-position to the azo-group. By sodium sulphide in alcoholic solution they are reduced to benzeneazonitrodiaminodiarylamines of the general formula,



4′-*Benzeneazo*-2 : 4-*dinitro*-3′-*aminodiphenylamine*, $NPh:N \cdot C_6H_3(NH_2) \cdot NH \cdot C_6H_3(NO_2)_2$, obtained by the action of 1-chloro-2 : 4-dinitrobenzene on 4-benzeneazo-1 : 3-diaminobenzene (chrysoidine), crystallises in bright red needles, m. p. 187°, and gives a violet solution in concentrated sulphuric acid; its *acetyl* compound forms slender, orange-red needles, m. p. 218°, and its *benzoyl* compound, silky, red needles, m. p. 241°. *N*-Phenyl-2′ : 4′-*dinitrophenylamino*(3)*benztriazole* (formula II, above), crystallises in slender, yellow needles, m. p. 188°, and dissolves in concentrated sulphuric acid giving a reddish-yellow coloration.

4′-p-*Chlorobenzeneazo*-2 : 4-*dinitro*-3′-*aminodiphenylamine*, $C_6H_4Cl \cdot N:N \cdot C_6H_3(NH_2) \cdot NH \cdot C_6H_3(NO_2)_2$, prepared from 4-*p*-chlorobenzeneazo-1 : 3-diaminobenzene, forms lustrous, reddish-brown leaflets, m. p. 220°, and gives a blue solution in concentrated sulphuric acid.

4-p-*Chlorobenzeneazo*-1 : 3-*diaminobenzene* (p-*chlorochrysoidine*), $C_6H_4Cl \cdot N:N \cdot C_6H_3(NH_2)_2$, prepared by the interaction of *p*-chlorophenyldiazonium chloride on *m*-phenylenediamine hydrochloride, crystallises in lustrous, yellow needles, m. p. 140°, and its *hydrochloride* in slender, red needles, m. p. 225°. 4-p-*Bromobenzeneazo*-1 : 3-*diaminobenzene* (p-*bromochrysoidine*), $C_{12}H_{11}N_4Br$, similarly prepared, forms lustrous, golden-yellow needles, m. p. 155°, and its *hydrochloride* red needles, m. p. 213°. 4′-p-*Bromobenzeneazo*-2 : 4-*dinitro*-3′-*aminodiphenylamine*, $C_{18}H_{13}O_4N_6Br$, prepared from the preceding compound, forms lustrous, brick-red needles, m. p. 218°, and dissolves in concentrated sulphuric acid, giving a blue coloration.

4′-*Benzeneazo*-2 : 4-*dinitro*-3′-*amino*-6′-*methyldiphenylamine*, $NPh:N \cdot C_6H_2Me(NH_2) \cdot NH \cdot C_6H_3(NO_2)_2$, forms deep red needles, m. p. 273—274°, and dissolves to an emerald-green solution in concentrated sulphuric acid; its *acetyl* derivative forms orange-yellow needles, m. p. 196°, and its *benzoyl* derivative, orange-red needles, m. p. 252°. 4′-*Benzeneazo*-4-*nitro*-2 : 3′-*diamino*-6′-*methyldiphenylamine*, $C_{19}H_{18}O_2N_6$, formed on reduction of the preceding compound by means of sodium sulphide and alcohol, crystallises in lustrous, garnet-red prisms with metallic reflection, m. p. 244°.

4-p-*Chlorobenzeneazo*-1 : 3-*diamino*-6-*methylbenzene* (p-*chloromethylchrysoidine*), $C_6H_4Cl \cdot N:N \cdot C_6H_2Me(NH_2)_2$, prepared from *p*-chlorophenyldiazonium chloride and *m*-tolylenediamine hydrochloride, forms lustrous, golden-yellow leaflets, m. p. 169°, and its *hydrochloride*, lustrous, red needles, m. p. 235°. 4′-p-*Chlorobenzeneazo*-2 : 4-*dinitro*-3′-*amino*-6′-*methyldiphenylamine*, $C_{19}H_{15}O_4N_6Cl$, prepared from the preceding compound, crystallises in reddish-brown, lustrous needles, m. p. 286°, and dissolves in concentrated sulphuric acid, giving a green coloration; its *acetyl* compound forms slender, orange-yellow needles, m. p. 248°, and its *benzoyl* compound, orange needles, m. p. 285°. On reduction with sodium sulphide in alcoholic solution, it gives 4′-p-*chlorobenzeneazo*-4-*nitro*-

2 : 3′-*diamino-6′-methyldiphenylamine*, $C_{19}H_{17}O_2N_6Cl$, which forms slender, reddish-brown crystals, m. p. 262°. 4-p-*Bromobenzeneazo-1 : 3-diamino-6-methylbenzene* (p-*bromomethylchrysoidine*),

$$C_{13}H_{13}N_4Br,$$

crystallises in lustrous, golden-yellow leaflets, m. p. 177°, and its *hydrochloride* in lustrous, red needles, m. p. 236°. 4′-p-*Bromobenzeneazo-2 : 4-dinitro-3′-amino-6′-methyldiphenylamine*,

$$C_{19}H_{15}O_4N_6Br,$$

prepared from the preceding compound, crystallises in brownish-red leaflets, m. p. 290°, and yields a green solution in sulphuric acid; its *acetyl* derivative forms orange needles, m. p. 242°, and its *benzoyl* derivative, orange-yellow needles, m. p. 275°. 4′-p-*Bromobenzeneazo-4-nitro-2 : 3′-diamino-6′-methyldiphenylamine*,

$$C_{19}H_{17}O_2N_6Br,$$

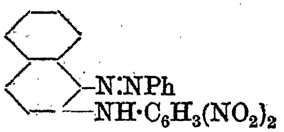
forms reddish-brown leaflets, m. p. 265°.

4-α-*Naphthaleneazo-1 : 3-diamino-6-methylbenzene*,

$$C_{10}H_7{\cdot}N{:}N{\cdot}C_6H_2Me(NH_2)_2,$$

prepared from α-naphthyldiazonium chloride on *m*-tolylenediamine hydrochloride, crystallises in brown needles with green, metallic reflection, m. p. 148°. 4′-α-*Naphthaleneazo-2 : 4-dinitro-3′-amino-6′-methyldiphenylamine*, $C_{10}H_7{\cdot}N{:}N{\cdot}C_6H_2Me(NH_2){\cdot}NH{\cdot}C_6H_3(NO_2)_2$, obtained from the preceding compound, forms reddish-brown needles with violet metallic reflection, m. p. 286°; its *acetyl* compound forms red needles, m. p. 268°, and its *benzoyl* compound, yellow needles, m. p. 246°. 4′-α-*Naphthaleneazo-4-nitro-2 : 3′-diamino-6′-methyldiphenylamine*, $C_{23}H_{20}O_2N_6$, forms reddish-brown needles, m. p. 214°. 4-β-*Naphthaleneazo-1 : 3-diamino-6-methylbenzene* (β-*naphthylmethylchrysoidine*), $C_{17}H_{16}N_4$, crystallises in yellow needles, m. p. 242°. 4-β-*Naphthaleneazo-2 : 4-dinitro-3′-amino-6′-methyldiphenylamine* forms a reddish-brown, crystalline powder, chars, without melting, above 300°, and gives a green solution in concentrated sulphuric acid; its *acetyl* compound separates in slender, yellow needles, m. p. 272°, and its *benzoyl* compound in orange needles, m. p. 267°. 4-β-*Naphthaleneazo-4-nitro-2 : 3′-diamino-6′-methyldiphenylamine*, $C_{23}H_{20}O_2N_6$, forms minute, reddish-brown crystals, m. p. 261°.

α-*Benzeneazo-β-naphthyl-2 : 4-dinitrophenylamine* (annexed formula), prepared by the action of 1-chloro-2 : 4-dinitrobenzene on α-benzeneazo-β-naphthylamine, crystallises in slender, red needles, m. p. 285°, and gives a greenish-blue solution in concentrated sulphuric acid. α-*Benzeneazo-β-naphthyl-4-nitro-2-aminophenylamine*, $NPh{:}N{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_3(NH_2){\cdot}NO_2$, forms reddish-brown needles, m. p. 147°.



α-o-*Tolueneazo-β-naphthyl-2 : 4-dinitrophenylamine*, $C_{23}H_{17}O_4N_5$, obtained from α-*o*-tolueneazo-β-naphthylamine, crystallises in slender, red needles, m. p. 223°, and dissolves in concentrated sulphuric acid to a greenish-blue solution. α-m-*Tolueneazo-β-naphthylamine* has m. p. 103—104°. α-m-*Tolueneazo-β-naphthyl-2 : 4-dinitrophenylamine* forms slender, red needles, m. p. 245°, and gives a greenish-blue solution in concentrated sulphuric acid. α-m-*Tolueneazo*-β-*naphthyl*-4-*nitro*-2-*aminophenylamine*, $C_{23}H_{19}O_2N_5$, is obtained as a dark red, microcrystalline powder, m. p. 116°. α-p-*Tolueneazo*-β-*naphthyl*-2 : 4-*dinitrodiphenylamine* crystallises in slender, red needles, m. p. 280°, and dissolves in concentrated sulphuric acid to a green solution. α-p-*Tolueneazo*-β-*naphthyl*-4-*nitro*-2-*aminophenylamine* forms microscopic, reddish-brown crystals, m. p. 155°.

α-p-*Chlorobenzeneazo*-β-*naphthyl*-2 : 4-*dinitrophenylamine*, $C_{22}H_{14}O_4N_5Cl$, crystallises in slender, bright red needles, m. p. 278°, and dissolves in concentrated sulphuric acid to a deep blue solution. α-p-*Bromobenzeneazo*-β-*naphthylamine*, $C_6H_4Br{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH_2$, forms red crystals, m. p. 135—136°. α-p-*Bromobenzeneazo*-β-*naphthyl*-2 : 4-*dinitrophenylamine* crystallises in slender, red needles, m. p. 263°, and gives a deep blue solution in concentrated sulphuric acid. 4-*Benzeneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine*, obtained from 4-benzeneazo-α-naphthylamine, forms long, bright-red, silky needles, m. p. 200°, and colours concentrated sulphuric acid bright blue. 4-*Benzeneazo*-α-*naphthyl*-4-*nitro*-2-*aminophenylamine* separates in minute, reddish-brown crystals, m. p. 181°, and its *acetyl* compound slender, red needles, m. p. 216°.

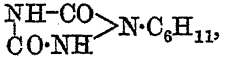
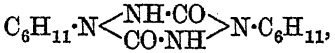
4-o-*Tolueneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine*, $C_6H_4Me{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_3(NO_2)_2$, forms lustrous, reddish-brown crystals, m. p. 224°, and dissolves in concentrated sulphuric acid to a deep blue solution. 4-p-*Tolueneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine* crystallises in lustrous, bright red needles, m. p. 207°, and gives a blue solution in concentrated sulphuric acid. 4-p-*Tolueneazo*-α-*naphthyl*-4-*nitro*-2-*aminophenylamine* separates in reddish-brown crystals, m. p. 200°.

4-o-*Nitrobenzeneazo*-α-*naphthylamine*, $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH_2$, crystallises in slender, metallic green needles, m. p. 165°. 4-o-*Nitrobenzeneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine*, $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_3(NO_2)_2$, forms a reddish-brown, microcrystalline powder, m. p. 212°, and yields a blue solution in concentrated sulphuric acid. 4-p-*Nitrobenzeneazo*-α-*naphthylamine* crystallises in deep red needles with metallic reflection, m. p. 252°. 4-p-*Nitrobenzeneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine* separates in slender, brownish-red needles, m. p. 263°, and dissolves in concentrated sulphuric acid giving a violet coloration.

4-p-*Chlorobenzeneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine*, $C_{22}H_{14}O_4N_5Cl$, forms slender, orange needles, m. p. 258°, and gives a green solution in concentrated sulphuric acid. 4-p-*Chlorobenzeneazo*-α-*naphthyl*-4-*nitro*-2-*aminophenylamine* separates in slender, deep red crystals, m. p. 228°.

4-α-*Naphthaleneazo*-α-*naphthyl*-2 : 4-*dinitrophenylamine*, $C_{10}H_7{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_3(NO_2)_2$, crystallises in slender, brownish-red needles, m. p. 203°, and dissolves to a blue solution in concentrated sulphuric acid. 4-β-*Naphthaleneazo-α-naphthyl*-2 : 4-*dinitrophenylamine* forms reddish-brown needles, m. p. 241°, and dissolves in concentrated sulphuric acid giving a blue solution. T. H. P.

Reduction of Semicarbazones. E. J. Poth and J. R. Bailey (*J. Amer. Chem. Soc.*, 1923, **45**, 3001—3008; cf. A., 1922, i, 880).—Semicarbazones were reduced to the corresponding semicarbazides under a pressure of $1\frac{2}{3}$—$2\frac{1}{3}$ atm. of hydrogen in the presence of colloidal platinum. The minimum proportion of platinum necessary for efficient reaction varied considerably and when the reduction produced a basic substance the yield was increased by the addition of acid; the amount of acid required varied greatly. The following semicarbazides were prepared. *Fenchylsemicarbazide*, short needles, m. p. 181°. *Benzoylfenchylsemicarbazide*, a crystalline powder, decomp. 226°. *α-Phenylcarbamylfenchylsemicarbazide*, thin plates, m. p. 192°. *Carvomenthylsemicarbazide*, thin plates, m. p. 126° (decomp.), and its *hydrochloride*, short needles, decomp. 186°. *Benzoylcarvomenthylsemicarbazide*, m. p. 235°. *α-Phenylcarbamylcarvomenthylsemicarbazide*, clusters of radiating needles, m. p. 205°. cyclo*Hexylsemicarbazide*, needles, decomp. 185°, and its *hydrochloride*, m. p. 176—178°. *Benzoyl*cyclo*hexylsemicarbazide*, fine needles, m. p. 267° (decomp.). *α-Phenylcarbamyl*cyclo*hexylsemicarbazide*, microscopic short needles, decomp. 236°. Benzylsemicarbazide. *Benzoylmenthylsemicarbazide*, a crystalline powder, m. p. 216° (decomp.). *α-Phenylcarbamylmenthylsemicarbazide*, radiating needles, decomp. 184°. In the preparation of *iso*propyl, bornyl, and menthyl semicarbazides the proportion of colloidal platinum may be considerably reduced with advantage. The following triazoles were obtained by boiling the corresponding acyl semicarbazide with caustic alkali. 3-*Hydroxy*-5-*phenyl*-1-*fenchyltriazole*, thick, triangular plates, m. p. 234°. 3-*Hydroxy*-5-*phenyl*-1-*carvomenthyltriazole*, thin plates, m. p. 187°. 3-*Hydroxy*-1-cyclo*hexyl*-5-*phenyltriazole*, slender prisms, m. p. 232—234°. F. B.

Behaviour of Semicarbazides at Elevated Temperatures. E. J. Poth and J. R. Bailey (*J. Amer. Chem. Soc.*, 1923, **45**, 3008—3012; cf. preceding abstract).—cyclo*Hexylsemicarbazide*, when heated at 200° during twelve minutes yielded *di*cyclo*hexylcarbazide* (I), $CO(NH{\cdot}NH{\cdot}C_6H_{11})_2$, plates, m. p. 187°, and unchanged semicarbazide. When the semicarbazide was heated for one and a half hours at 180—185° the products were cyclo*hexylurazole* (II)  $\begin{matrix}NH{-}CO\\ CO{\cdot}NH\end{matrix}{>}N{\cdot}C_6H_{11}$, thin, prismatic plates, m. p. 271°, and *di*cyclo*hexylurazine* (III),  $C_6H_{11}{\cdot}N{<}\begin{matrix}NH{\cdot}CO\\ CO{\cdot}NH\end{matrix}{>}N{\cdot}C_6H_{11}$, needles or prisms, m. p. 197°; (I) was obtained in good yield when the semicarbazide was mixed with half its weight of urethane and heated at 160°, (II) was prepared by heating the semicarbazide and carbamide in molecular proportions, and (III) by decomposing the hydrochloride of the corresponding semicarbazide. F. B.

Arylazides. I. Conversion of *p*-Methylarylazides into Homologues of Quinol in Presence and Absence of Phenol. E. BAMBERGER and J. BRUN (*Helv. Chim. Acta*, 1923, 6, 935—941).—Some further experiments on the conversion of arylazides into homologues of quinol (cf. A., 1921, i, 716) are described. *p*-Tolylazide (5 g.) boiled with dilute sulphuric acid (1 : 3 by volume) gives about 1 g. of toluquinol, with some *p*-toluidine, a strong odour of cresol, but no aminocresol. From 25 g. of *m*-4-xylylazide, boiled for nine hours with dilute sulphuric acid, there were obtained 1·8 g. 1 : 3-dimethylquinol, 0·2 g. *as*-*m*-xylenol, 4·2 g. *as*-*m*-xylidine, and a considerable quantity of amorphous acids, bases, and resin. When *p*-tolylazide was boiled as before in dilute acid in presence of excess of phenol, from 6 g. of azide, 4·27 g. of *p*-hydroxyphenyl-*p*-tolylamine was obtained, and about 0·32 g. of toluquinol. The theory of the reactions involved has been previously discussed (*loc. cit.*).

E. H. R.

Arylazides. II. The Conversion of *p*-Methylarylazides into Imino-ψ-quinols and ψ-Quinols. E. BAMBERGER and J. BRUN (*Helv. Chim. Acta*, 1923, 6, 942—951).—Practical details are given of experiments previously reported (A., 1921, i, 716).

E. H. R.

Partial Decomposition of Proteins. E. ABDERHALDEN (*Z. physiol. Chem.*, 1923, **131**, 284—295).—A general description is given of the method of isolating the products of the partial hydrolysis of proteins. The protein is treated with 70% sulphuric acid at a low temperature, *e.g.*, at the ordinary temperature, or at blood heat, and the course of hydrolysis is followed by estimating the amino-nitrogen and comparing it with the total nitrogen, of which an estimation is made on the original protein. The sulphuric acid is removed as barium sulphate, and the filtrate is concentrated in a vacuum. If the product is a solid, it is extracted directly with ether in a Soxhlet apparatus; if it is a syrup, it is mixed with sand to a thick consistency and then extracted. It is afterwards extracted in turn with ethyl acetate, acetone, or methyl alcohol, and if necessary with other solvents such as chloroform or butyl alcohol. It is usually possible after evaporation of the solvent to obtain the fractions in a crystalline form, and they are purified according to their particular composition. In particular cases, variations at any stage may be advisable.

In an attempt to obtain the maximum yield of *d*-alanylglycine anhydride from silk clippings, the residue after hydrolysis, removal of sulphuric acid, and concentration, was treated with alcohol and hydrogen chloride, evaporated to dryness, and the residue dissolved in alcohol. The ammonium chloride separating at once on saturation with ammonia was filtered off. On keeping at 37°, a series of crystalline fractions was obtained, which were extracted in a Soxhlet apparatus with ethyl acetate. Eighty-five g. of pure glycylalanine anhydride was obtained from 1 kg. of silk clippings. Small quantities of glycyl-*l*-tyrosine anhydride and of *d*-alanyl anhydride (dimethylpiperazine) were also obtained.

One kg. of casein was hydrolysed with 10% sulphuric acid at 80°, and the product extracted with ethyl acetate, when 2·5 g. of crystals were obtained, decomp. 280°, and this compound proved to be *l*-leucyl-*d*-valine anhydride. On extracting the residue from the ethyl acetate extraction with acetone, crystals were obtained which on hydrolysis yielded leucine, valine, and glutamic acid, but there was no guarantee that the compound was pure. On further extraction with methyl alcohol, *d*-alanyl-*l*-leucine was obtained along with a crystalline *compound*, $C_{14}H_{23}O_3N_3$, m. p. 192°, $[\alpha]$ −183°, which yielded proline, *l*-leucine, and *d*-alanine on hydrolysis. It is apparently an anhydride formed from these acids by the elimination of 3 mols. of water. W. O. K.

The Formation of Carbon Dioxide during the Breakdown of Proteins in the Autoclave. V. S. Sadikov (*Biochem. Z.*, 1923, **143**, 492—495).—The method used for the catalytic hydrolysis of proteins by dilute hydrochloric acid under pressure (A., 1923, i, 867) leads in the case of gelatin to a slight formation of carbon dioxide amounting to 2% of the protein. It is suggested that this arises by decarboxylation of the amino-acids under the conditions used. Increasing pressure favours carbon dioxide formation. Nitrogen is also present in the residual gas in the autoclave and oxygen is largely absorbed during the process. J. P.

Hydrolysis in an Autoclave containing Nitrogen. V. S. Sadikov (*Biochem. Z.*, 1923, **143**, 496—503).—Arising from the author's work on the catalytic hydrolysis of proteins under pressure (cf. preceding abstract), it is found that a retention of nitrogen results when this is carried out in an atmosphere of the gas. Dextrose gives negative results, but a fixation is observed in the case of aspartic acid and to a less extent in the case of glycine. Similar treatment of fumaric and succinic acids in the autoclave leads to a notable retention of nitrogen, which is ascribed to the unsaturated compounds arising from these acids. J. P.

Separation of Proteins of White of Egg by the Acetone Method. M. Piettre (*Compt. rend.*, 1924, **178**, 91—93).—Details are given for the separation of the proteins of white of egg into a globulin, ovalbumin (coagulating at 52·5—53°, and having α_D −41·25°), and a glucoprotein. The latter (α_D −62·47°) reduces boiling Fehling's solution, and, at a moderate temperature, mercury and bismuth salts (in presence of alkali) and ammoniacal silver nitrate. E. E. T.

A Further Method of Determining the Isoelectric Point of Proteins and its Application to the Serum-albumins of Various Animals. L. Michaelis and T. Nakashima (*Biochem. Z.*, 1923, **143**, 484—491).—The optimum precipitation point of a mixture of mastic and gelatin in the presence of an acetate buffer approaches the isoelectric point of the latter as its relative amount is increased. This observation is made the basis of a method of determining the isoelectric points of various serum-albumins. To a series of tubes containing mastic sol and an acetate buffer at varying known p_H, increasing amounts of the albumin are added, and the p_H of the zone of optimum precipitation is observed to rise to a constant value beyond which addition of the albumin produces no further shift. This maximum p_H corresponds with the isoelectric point. The following values for the albumins examined were found: ox and guinea-pig, 4·65; dog, 4·66; puppy, 4·67; turtle and man, 4·68. J. P.

Nature of the Reaction between Carbophosphide and Blood-serum. G. Cuneo (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 294—298; cf. this vol., i, 100).—The interaction of carbophosphide and blood-serum yields a phospho-albumin which contains phosphorus in organic combination and either in the most highly oxidised state or as metaphosphoric acid. Since, further, nuclein bases occur among its products of hydrolysis, this phospho-albumin probably owes its existence to a hydrolytic process coupled with atmospheric oxidation, as a result of which the phosphorus of the carbophosphide enters the protein molecule as phosphoric oxide or as a hydrate of the latter. T. H. P.

Nature of the Reaction between Carbophosphide and Blood-serum. G. Cuneo (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 353—357; cf. this vol., i, 100, and preceding abstract).—The author has now investigated the behaviour of blood-serum towards a number of different compounds, some free from, and others containing phosphorus. Certain of these compounds do not denature the serum albumin molecule, which remains phosphorus-free, normally digestible by gastric juice, and without hindering effect on putrefactive processes. On the other hand, phosphorus di-iodide, ethylphosphine, and sodium hypochlorite effect denaturation of the protein molecule, the reaction, like that produced by carbophosphide, being probably of the nature of an auto-oxidation. The reaction of the serum-albumin with hypochlorite is complex, but the principal product is devoid of iron and phosphorus and exhibits the chemical and biological properties of the nucleic acids. T. H. P.

Formation of Methæmoglobin. II. W. Heubner and H. Rhode. **III.** R. Meier. **IV.** W. Heubner and R. Meier. **V.** W. Heubner, R. Meier, and H. Rhode (*Arch. expt. Path. Pharm.*, 1923, **100**, 117—127, 128—136, 137—148, 149—161).—I. A comparison of various substances which convert oxyhæmoglobin into methæmoglobin shows that the actions of potassium ferricyanide and of *p*-benzoquinone are almost identical in this respect.

Although the compound of hæmoglobin with nitric oxide is resistant to the action of reducing agents, it may be decomposed by means of indifferent gases and also by dialysis.

II. Optical and gasometric observations show that by the use of ferricyanide or of *p*-benzoquinone in varying proportions it is possible to produce a mixture of oxyhæmoglobin and methæmoglobin with the two constituents in any desired proportions. The last traces of oxyhæmoglobin are converted into methæmoglobin more easily by ferricyanide than by *p*-benzoquinone.

III. In the presence of hæmoglobin, quinol, *p*-aminophenol and hydrazobenzene are rapidly oxidised by atmospheric oxygen. Whereas the oxidation products of the first two of these substances are active in forming methæmoglobin, that of hydrazobenzene is not; the formation of methæmoglobin by hydrazobenzene therefore, must be due to an activation of the atmospheric oxygen in the process of oxidation of this substance.

Nitrosobenzene converts oxyhæmoglobin in part into methæmoglobin and in part into reduced hæmoglobin.

IV. Phenylhydroxylamine converts oxyhæmoglobin into methæmoglobin and is itself simultaneously converted into azoxybenzene; excess of phenylhydroxylamine in this reaction reduces the methæmoglobin first formed to hæmoglobin. Reduced hæmoglobin is unaltered optically by phenylhydroxylamine.

m-Nitrophenylhydroxylamine reacts similarly to phenylhydroxylamine but not so strongly. C. R. H.

The Natural Porphyrins. IV. Ooporphyrin. HANS FISCHER and F. KÖGL (*Z. physiol. Chem.*, 1923, **131**, 241—261).—Three hundred g. of gull's egg-shells were extracted with methyl alcohol containing hydrogen chloride, the extract was concentrated, made alkaline with sodium carbonate, and the precipitate washed and dried at 100°. The material was extracted with chloroform, which was then distilled off, and the residue dissolved in a little chloroform, precipitated by the addition of light petroleum, collected on a filter, and dried. It was then again dissolved in a little chloroform, and boiling methyl alcohol was added. *Ooporphyrin dimethyl* ester, $C_{34}H_{36}O_2N_4(OMe)_2$, was obtained as leaflets grouped in rosettes, m. p. 225—230°. The absorption bands of this compound are described at length. They resemble those of Kammerer's porphyrin. When ooporphyrin methyl ester from the shell of the gull or of the plover egg is treated with powdered iron in boiling acetic acid, crystals are obtained which although similar, are not identical, crystallographically and spectroscopically. The absorption bands of solutions of ooporphyrin from the egg-shells of various species of birds are described. W. O. K.

The Precipitation of the Lactoproteins by Copper Salts. A. J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1923, **32**, 376—386). —The lactoproteins have been precipitated by the addition of various salts of copper (sulphate, chloride, nitrate, and acetate) and the effect of washing the precipitates by water has been examined. With the sulphate, chloride, and nitrate, the results obtained are practically identical. Apart from the case of the acetate precipitate, washing by water appears to have no influence on the composition of the precipitate and its copper content. A second series of experiments was carried out to determine the composition of the solid and liquid phases forming the primitive complex, The results obtained show that the quantity of copper in the precipitates increases as the initial concentration of the copper increases, whilst the ratio of the quantity of copper precipitated to the total quantity of copper employed diminishes, generally in proportion as the initial concentration of the copper increases. The anion present is shown to have a visibly marked effect on the precipitation of the metallic kation. Galeotti's conclusions (A., 1904, i, 355) as to the equilibrium between the proteins and sulphate of copper are not upheld. F. G. P.

Triphosphonucleic Acid and Thymic Acid. S. J. THANNHAUSER (*Z. physiol. Chem.*, 1923, **131**, 296—303; cf. Feulgen and Rosenbeck, A., 1923, i, 618, and Feulgen, *ibid.*, i, 964; also Thannhauser and Sachs, A., 1920, i, 201).—The author has found that after hydrolysing triphosphonucleic acid by alkali, the adenosine may be precipitated as picrate and has obtained almost the theoretical yield of this picrate. He does not admit the validity of the criticism of Feulgen (*loc. cit.*), who doubts the existence of the acid, but he considers that triphosphonucleic acid is with great probability a pure substance. The author also criticises the results of Feulgen (cf. *loc. cit.*) regarding thymic acid. W. O. K.

Influence of Time on the Physico-chemical Properties of Gelatin Solutions. R. DE IZAGUIRRE (*Kolloid Z.*, 1923, **33**, 337—347).—The effect of time on the viscosity, multi-rotation, and the action of electrolytes on gelatin solutions has been examined. It is shown that in the presence of hydrochloric acid the influence of time on the viscosity of gelatin solutions passes through a minimum with increasing concentration of hydrochloric acid. This minimum corresponds with the initial viscosity of the solution. The same regularity is found with the time change of the osmotic pressure, whereby the change with time is smaller the larger the osmotic pressure. Since the maximum of the viscosity and the osmotic pressure is closely connected with the swelling, it follows that the time change takes place in the opposite sense to the swelling, that is, the greater the degree of swelling the smaller the time change. Since the viscosity serves as a measure of the gelatinisation this must be regarded as an "unmixing" process and not as the formation of a hypothetical new modification of the gelatin. The optical rotation of gelatin solutions increases with time in such a way that a curve plotted between the logarithm of the angle of rotation and the logarithm of the time is a straight line. The multirotation is expressed by the formula $[\alpha]_D = K.t^n$, in which for a 1% solution of gelatin $K=209$ and $n=0{\cdot}082$. J. F. S.

The Isoelectric Point of Gelatin from Hide and Bone. O. GERNGROSS and S. BACH (*Biochem. Z.*, 1923, **143**, 542—552).—The isoelectric points of various preparations of gelatin have been found to range from p_H 4·45 to 5·55 according to their source. [Cf. also *B.* Feb.] J. P.

The Displacement of the Isoelectric Point of Gelatin by Formaldehyde. O. GERNGROSS and S. BACH (*Biochem. Z.*, 1923, **143**, 533—542).—The isoelectric points of two preparations of gelatin were lowered from p_H 5·05 to 4·6 and from p_H 4·75 to 4·3, respectively, by the presence of formaldehyde. J. P.

Points of Minimum Swelling of Ash-free Gelatin. J. A. Wilson and E. J. Kern (*J. Amer. Chem. Soc.*, 1923, **45**, 3139—3140; cf. A., 1923, i, 68).—The two points of minimum in the curve showing the degree of swelling of gelatin as a function of the p_H value, namely at 4·7 and 7·7, were confirmed when using ash free gelatin. The points coincide with those at which minimum values for the wave-length of maximum absorption in the ultra-violet are observed. F. B.

Diffusion of Arsenic [Trioxide] in Gelatin. R. Schaefer (*Kolloid Z.*, 1923, **33**, 286—289).—A clear, transparent gel containing arsenious oxide and suitable for dental purposes, may be prepared by adding a few c.c. of hot 30% gelatin solution to a hot solution of arsenious oxide with vigorous stirring. The solution is evaporated slowly on a water-bath and every fifteen minutes a quarter of the evaporated water is replaced by gelatin solution. This process is continued until the concentration desired is reached and the whole allowed to cool to a clear gel. In this way, a gel containing 12—15% of arsenious oxide and 20—30% of gelatin is obtained. The diffusion of arsenious oxide in gelatin has been investigated by laying small portions of the above described gel, and a paste of the powdered oxide and water on a large piece of gelatin and, after sufficient time has elapsed, examining the gelatin by exposing it to hydrogen sulphide. In the case of the arsenic gel, it is found that the amount of arsenic diffused falls off quite regularly as the distance travelled increases, but with the paste there is no apparent diffusion beyond the surface of the gelatin, although this has undoubtedly taken place. The author is of the opinion that in the paste simple molecules are present, but in the gel more complicated molecules are present and these move more slowly, but the total amount of arsenic diffused is greater in the latter case than in the former. J. F. S.

Reaction of Alkaloids with Gelatin [Solutions] containing Iodine. H. Handovsky and E. du Bois-Reymond (*Kolloid Z.*, 1923, **33**, 347—348).—Liesegang rings are produced when a solution of 1 : 1000 pilocarpine hydrochloride is placed on a gel containing 3% of gelatin, 0·6% of potassium iodide, and 0·4% of iodine. The rings are alternately reddish-yellow and dark brown, and are about 1—2 mm. apart. Similar, but differently coloured, rings are produced with strychnine nitrate 1 : 1000 and papaverine hydrochloride 1 : 100. J. F. S.

The Composition of Spinning Silk. E. Abderhalden (*Z. physiol. Chem.*, 1923, **131**, 281—283).—From the product of the hydrolysis of spinning silk by 70% sulphuric acid at 37° there has been isolated glycyl-*l*-tyrosine anhydride, m. p. 282°, and glycyl-*d*-alanine anhydride, m. p. 245°. W. O. K.

The Influence of Temperature on the Action of Amylase. The Action on the Saccharifying Power of Amylase. T. CHRZĄSZCZ (*Biochem. Z.*, 1923, **142**, 417—439).—The influence of temperature on the activity of the amylases of various cereals at the optimum p_H of 4·9 is not uniform. The optimum ranges found are: for barley amylase 49—54°, for rye and wheat amylases 49—55°, for oats amylase 51—53°, and for buckwheat amylase 50—55°. In the cases of maize (56—57°) millet (58—59°), and African millet (62—64°) the optima quoted in brackets lie above the temperatures at which destruction of the enzyme begins. In aqueous solutions, barley amylase is inactivated at 61—62°, rye and wheat amylases at 63—64°, and the other varieties at 65—66°. In general, plant amylases are completely destroyed in one hour when exposed to a temperature of 75°. Amylases from the same genera but of different varieties show the same susceptibility to alteration of temperature at the optimum p_H. Aqueous malt extracts prepared by shaking for at least one hour give a precipitate when heated at 50°, but if the shaking be of shorter duration (thirty minutes), precipitation does not commence below 55—60°. The precipitate does not affect the activity of the enzyme. Rye-malt extract is exceptional in giving at most a slight opalescence even at 80°. J. P.

Potato Amylase. H. HAEHN and H. SCHWEIGART (*Biochem. Z.*, 1923, **143**, 516—526).—Potato amylase is activated by sodium chloride and fluoride, and by potassium, calcium, barium, and magnesium chlorides. It is inhibited by the salts of the heavy metals. Amino-acids have an activating effect (cf. Doby, *Biochem. Z.*, 1914, **67**, 166). Potato amylase after being freed from most of its salts by dialysis or ultra-filtration loses much, but not all, of its activity, but is reactivated by the addition of the salts of the alkali or alkaline-earth metals. A method of combined dialysis and ultra-filtration yields inactive, salt-free preparations of the amylase, which are reactivated by salts. It is concluded that potato amylase consists of an inactive organic constituent together with an indispensable activating mineral salt. J. P.

The Hexose Monophosphatase of Takadiastase. J. NOGUCHI (*Biochem. Z.*, 1923, **143**, 190—194).—A phosphatase is present in takadiastase which hydrolyses barium and sodium hexose monophosphates at 37°. In the former case, barium phosphate separates as a gel, and in the latter the extent of the hydrolysis, which may be practically quantitative, is dependent on the concentration of the enzyme. J. P.

The Cellase of Takadiastase. C. NEUBERG and O. ROSENTHAL (*Biochem. Z.*, 1923, **143**, 399—401).—Takadiastase contains a cellase which at 37° completely hydrolyses cellobiose to dextrose in five days. J. P.

Hemicellusose. IV. Cellobiase and Lichenase. H. PRINGSHEIM and J. LEIBOWITZ (*Z. physiol. Chem.*, 1923, **131**, 262—268).—Lichenin, which is hydrolysed to dextrose by malt extract, has been acetylated and then hydrolysed to octoacetylcellobiose (Karrer and Joos, A., 1923, i, 541). It ought therefore to be possible to show that malt extract hydrolyses it first to cellobiose by means of a lichenase, and then to glucose by cellobiase, *i.e.*, to show that both lichenase and cellobiase are present in malt extract. This is verified as cellobiose is hydrolysed to dextrose by malt extract at 37°, and p_H 5, and on the other hand, malt extract, after being kept for three months, hydrolyses lichenin only to cellobiose, as the cellobiase apparently disappears on keeping. The presence of cellobiose was determined by the determination of the reducing power and of the rotation of the solution, and also by the formation of the osazone. W. O. K.

Synthetic Action of α-*d*-Mannosidase in Presence of some Monohydric Alcohols. H. Hérissey and J. Cheymol (*Compt. rend.*, 1924, **178**, 123—125).—α-*d*-Mannosidase effects a partial conversion of mannose, in presence of ethyl, propyl, *iso*propyl, and *n*-butyl alcohols, into the corresponding *d*-mannosides (cf. A., 1923, i, 497). E. E. T.

The Separation of the Anti-neuritic Vitamin by Means of its Picrate. G. Bertrand and A. Seidell (*Bull. Soc. Chim. biol.*, 1923, **5**, 794—796).—The crude extract containing the active material is separated from inorganic substances as far as possible, dissolved in 60% alcohol and treated with a solution of picric acid in methyl alcohol. The crude picrate thus obtained is active in amounts of 2 mg. per diem when added to a diet of polished rice and administered to pigeons. On recrystallisation of the picrate from water two separate substances are obtained; one crystallises in needles, m. p. 202°, and is inactive; the other forms a crystalline powder, m. p. 160°, and is active. C. R. H.

Additive Products of the Phosphineimines. M. Masriera (*Anal. Fís. Quím.*, 1923, **21**, 418—435; cf. Staudinger and Hauser, A., 1922, i, 68).—The constitution of the additive products formed from phosphineimines and alkyl or acyl chlorides is discussed. Triphenylphosphinephenylimine reacts with acetyl chloride in ethereal solution, giving a white *compound* to which the formula $PPh_3\!:\!NPhAcCl$ is assigned. It is unstable and gives on decomposition acetanilide and triphenylphosphine oxide. The additive *compound* of triphenylphosphinephenylimine with methyl iodide is a white substance having m. p. 235°. Attempts to obtain addition of a second molecule of methyl iodide were unsuccessful. The additive *compound* of toluene-*p*-sulphonyl chloride with triphenylphosphineimine is a white, crystalline substance which decomposes when heated, forming resins. On keeping a mixture of triphenylphosphinephenylimine and toluene-*p*-sulphonyl chloride in ethyl-alcoholic solution for three months, two substances are obtained, namely, *triphenylphosphine*-p-*toluenesulphonylphenylammonium hydroxide*, $PPh_3\!:\!NPh(SO_2\cdot C_6H_4Me)\cdot OH$, a white crystalline substance, m. p. 191°, and its *isomeride*, for which the formula

$$OH\cdot PPh_3\cdot NPh\cdot SO_2\cdot C_6H_4Me$$

is suggested; it is crystalline and has m. p. 115°. G. W. R.

The Syntheses of Arsenic Acids by Means of Diazonium Salts. Z. Földi (*Ber.*, 1923, **56**, [*B*], 2489—2498).—Evidence is adduced in favour of the view that the diazonium arsenite is the primary product of Bart's arsinic acid synthesis (cf. Schmidt, A., 1920, i, 897). The transformation of the arsenious ion into the arsinic group is simply explained in accordance with Werner's theory if the constitution $H\left[\begin{matrix}OH\\ HO\cdot AsOH\\ OH\end{matrix}\right]$ or $H\left[OAs\begin{matrix}OH\\ OH\end{matrix}\right]$ is assigned to arsenious acid, and it is regarded as functioning as a monobasic acid, as is generally the case towards alkali kations including the diazonium-ion. In arsenious acid, the arsinic group exists therefore preformed. The production of the arsinate can therefore be explained by assuming that the diazonium kation present in the second sphere of the central arsenic atom enters the first sphere thereby transforming the tervalent into quinquevalent arsenic atom and that the diazoarsinic acid decomposes with evolution of nitrogen.

p-Toluidine is diazotised in hydrochloric acid solution by means of sodium nitrite; the cooled solution is saturated with hydrogen chloride, filtered to remove the precipitated sodium chloride, and treated with arsenic chloride, whereby a paste of colourless, granular crystals is produced without evolution of nitrogen. The product can be coupled with phenols or amines, thus showing the diazonium group to be intact. The addition of alkali hydroxide to the aqueous solution causes immediate evolution of nitrogen and the development of the colours and odours characteristic of Bart's reaction. In the presence of sodium hydrogen carbonate, the arsenious acid can be titrated with iodine, the end-point being shown by the formation of a dark coloured diazonium periodide. According to experimental conditions, the *compounds* $C_6H_4Me\cdot N_2Cl,AsCl_3$, $C_6H_4Me\cdot N_2Cl,2AsCl_3$, $C_6H_4Me\cdot N_2Cl,AsCl_2\cdot OH$, and $C_6H_4Me\cdot N_2Cl,AsCl_3,AsCl_2\cdot OH$ can be obtained. The first two of these are extremely labile and particularly sensitive to moisture; they can only be obtained from solutions which are completely saturated with hydrogen chloride. The fourth substance has m. p. 94—98° (decomp.); it readily loses hydrogen chloride and passes into the *pentachloro*-salt, $C_6H_4Me\cdot N_2(As_2Cl_5O)$, pale pink octahedra, m. p. 111—112° (decomp.), whereas when its solution in absolute alcohol is treated with anhydrous ether it gives the compound $C_6H_4Me\cdot N_2Cl,AsCl_2\cdot OH$, colourless crystals, m. p. about 90° (decomp.). The *salt*, $C_6H_4Me\cdot N_2(AsBr_3\cdot OH)$, m. p. 105°, is described. The hydroxy-chloro-salts can also be prepared from solid *p*-toluenediazonium chloride and arsenic trichloride in concentrated, absolute alcoholic solution.

The diazonium chloroarsenites decompose vigorously in aqueous or alcoholic solution, or in suspension in organic media with evolution of nitrogen in the presence of Gattermann's copper powder or cuprous chloride. In alcoholic solution, the reaction is very complex, giving di-*p*-tolyl, *p*-tolyl ethyl ether, arsenic acid, *p*-tolylarsinic acid, ethyl *p*-tolylarsinate, and *p*-tolylchloroarsine.

A study of the action of *p*-toluenediazonium sulphate on barium arsenite in the presence of water shows that diazonium arsenites are capable of existence in aqueous solution in the presence of an excess of arsenious acid, but attempts to obtain them in the solid state were not successful. Attempts to prepare solutions of diazonium arsenites in the absence of excess of arsenious acid are rendered difficult by the impossibility of preparing undecomposed diazonium hydroxide solutions. When, however, solutions of *p*-toluenediazonium sulphate, barium hydroxide, and arsenious acid in the molecular proportion 1 : 1 : 1 are mixed a pale yellow, turbid alkaline solution is obtained which is alkaline towards litmus but gradually becomes acidic; decomposition of the diazonium arsenite is shown to occur in accordance with the two schemes:

$$2C_6H_4Me{\cdot}N_2{\cdot}O{\cdot}As(OH)_2 = C_6H_4Me{\cdot}AsO(OH){\cdot}O{\cdot}N_2{\cdot}C_6H_4Me + N_2 + As(OH)_3$$ and

$$2C_6H_4Me{\cdot}N_2{\cdot}O{\cdot}As(OH)_2 = C_6H_4Me{\cdot}N_2{\cdot}AsO(OH){\cdot}O{\cdot}N_2{\cdot}C_6H_4Me + As(OH)_3,$$

the second being the more important. H. W.

Physiological Chemistry.

The Influence of Various Carbohydrates and Amino-acids on the Blood and Urinary Sugar of the Healthy Organism. A. SCHÄTTI (*Biochem. Z.*, 1923, **143**, 201—220).—In general, the ingestion by normal individuals of 20 g. of the following carbohydrates produces a hyperglycæmia the intensity of which diminishes in the order given: dextrose, lævulose, sucrose, lactose, galactose. The same amounts of starch, glycine, and alanine produce no hyperglycæmia, but after the ingestion of 100 g. of starch the rise in blood-sugar is as great as, but more delayed than, that produced by 100 g. of dextrose. Peptone and coffee give no hyperglycæmia. Lævulose is excreted more quickly and in greater amount than dextrose, and the sugar excreted after ingestion of sucrose consists chiefly of lævulose. Galactose seems to be excreted largely unchanged by the kidneys. Glycosuria following ingestion of dextrose increases with increasing hyperglycæmia, but the former shows a more delayed maximum than the latter. Glycosuria is not dependent on diuresis, but is regarded as a secretory process. J. P.

Blood-clotting as an Agglutination Process. E. HEKMA (*Biochem. Z.*, 1923, **143**, 105—110).—A theoretical paper in which the view is advanced, as a result of the author's previous work, that fibrin formation is a crystallisation process involving the dehydration and agglutination of fibrinogen amicrons. Thrombin is regarded, not as a fibrin ferment, but as an agglutinin, and fibrin consists of fibrinogen plus agglutinin. J. P.

The Influence of Chemicals on Erythrocyte Membranes by Changes in Corpuscular Volume. B. S. NEUHAUSEN and J. E. BRESLIN (*Bull. Johns Hopkins Hosp.*, 1923, **34**, 199—201).—A study of the effects of the salts of the blood and of dextrose on the erythrocyte membranes as shown by a comparison of cell volumes in iso-osmotic solutions. Ions cause swelling in the order, $Ca < Na < K$. The contracting action of calcium, as opposed to the swelling action of potassium, is specially pointed out. In the case of blood-corpuscles, the membranes are very complex colloidal mixtures, the swelling or precipitation of any component of which will loosen the whole structure.

CHEMICAL ABSTRACTS.

The Rôle of Pancreatic Juice in the Digestion of Proteins. Relative Importance of Trypsin and Erepsin. E. F. TERROINE and ST. J. PRZYLECKI (*Arch. internat. physiol.*, 1923, **20**, 377—396; *Ber. ges. Physiol.*, 1923, **20**, 64; from *Chem. Zentr.*, 1923, iii, 1290).—Pancreatic juice not activated by kinase attacks the normal products of gastric digestion. With activation by kinase, the action is increased. The relative importance of erepsin and trypsin depends on the degree of previous gastric digestion; where this is small, trypsin plays the more important part, but is less important where gastric digestion is more complete. As pancreatic digestion proceeds, the effect of trypsin recedes relative to that of erepsin.

G. W. R.

Effect of Magnesium Sulphate and Metallic Magnesium on Metabolic Exchanges. R. REDING and A. SLOSSE (*Compt. rend. Soc. biol.*, 1923, **88**, 644—646; from *Chem. Zentr.*, 1923, iii, 1108). —Intramuscular injection of 70 c.c. of 10% magnesium sulphate solution decreases the output of total nitrogen, uric acid, and sodium chloride, whilst the output of magnesium is increased. In a rectal carcinoma, injection of 20 c.c. of 10% magnesium sulphate solution was followed by decreased output of total nitrogen, amino-nitrogen, and sodium chloride, and increased output of uric acid and creatine. Similar effects were observed in a rabbit after introduction under the skin of a piece of metallic magnesium.

G. W. R.

The Internal Secretion of the Genital Organs. I. The Genital Organs and Carbohydrate Metabolism. S. TSUBURA (*Biochem. Z.*, 1923, **143**, 248—290).—Castration has no effect on the blood-sugar of fasting dogs, but in the sexually mature animal the operation produces a lowered sugar tolerance. The same effect is produced by ligature of one spermatic cord and extirpation of the opposite testicle, by ligature of both cords, or by exposing the genital glands to *X*-rays. These operations produce a degeneration of the sperm-cells, but do not affect the interstitial cells. The lowered sugar tolerance may be temporarily raised by transplantation of the sexual organs of another animal, but not by feeding the organs or by injection of extracts. Glycogen formation, glycogenolysis, and glycolysis of the blood-sugar in vitro are somewhat delayed after castration, but the blood amylase is unchanged.

After castration, the reactions of the blood-sugar to adrenaline, diuretin, and pituitrin are increased, but thyroid feeding has no effect, although it raises the low sugar tolerance of the castrated animals. The kidneys of the latter are more permeable to sugar, but the excretion of phenolsulphonephthalein is delayed as compared with the normal condition. In general, parallel experiments on male and female dogs gave similar results. The other endocrine organs show alterations after castration, and the observed results may not be wholly due to disturbances of the internal secretory functions of the genital organs. J. P.

The Internal Secretion of the Genital Organs. II. The Genital Organs and Respiratory Gaseous Metabolism. S. Tsubura (*Biochem. Z.*, 1923, **143**, 291—322).—Castration produces a lowered gaseous metabolism which becomes apparent about one month after the operation. A similar effect is produced by ligature of one spermatic cord and removal of the opposite testicle. Transplantation of the testes of another animal raises the gaseous exchange whilst feeding experiments are ineffective. Dogs in heat show no increased gaseous metabolism. Thyroid feeding raises the low gaseous exchange of castrated animals. The combined results of thyroid feeding on the sugar tolerance (cf. preceding abstract) and gaseous metabolism of castrated dogs are explained as being due to a moderate stimulation of the sluggish carbohydrate metabolism by the thyroid hormone. J. P.

The Ferments in the Placenta. K. Maeda (*Biochem. Z.*, 1923, **143**, 347—364).—Extracts of the placenta contain diastase in considerable amount, in part derived from the parental blood. Carboxylase and small quantities of lactase and invertase are present, but glycolytic enzymes are not found. Of proteolytic enzymes, erepsin, a weak trypsin, and traces of pepsin, but no rennin, are found. An asparagine deaminase is present. Mono- and tributyrases are found, and the latter, being stable to both quinine and atoxyl, is thus differentiated from serum lipase. Histozyme, a feeble salicylase, and an oxydase acting on pyrocatechol, adrenaline, and dihydroxyphenylalanine, but not on tyrosine, are present.

J. P.

The Site of Origin of Bilirubin. A. R. Rich (*Bull. Johns Hopkins Hosp.*, 1923, **34**, 321—329).—Hæmoglobin introduced into the blood-stream of a dog without a liver, and circulating actively for as long as five and a half hours is not transformed into bilirubin. Since, however, the production of bilirubin from circulating hæmoglobin takes place rapidly and readily in a dog with a liver through which the blood-stream passes, it is concluded that the liver is necessary for the transformation of circulating hæmoglobin into bilirubin. The conclusions are applicable only to hæmoglobin circulating in the blood-stream, not to hæmoglobin liberated into the tissues from extravasated blood; the conversion of hæmorrhage hæmoglobin into bilirubuin (hæmatoidin) is a purely local phenomenon, the exact mechanism of which is unknown.

Chemical Abstracts.

[Fish] Liver Oils. M. Tsujimoto (*J. Chem. Ind. Japan*, 1923, **26**, 482—486).—The oil from the Jewfish (*Stereolepis ischinagi* (Hilg.), contains a large amount of peculiar unsaponifiable matter (up to 50%), which is a viscous substance of reddish-orange colour, having a resinous odour, and showing much resemblance to colophony when dried at 100° for several hours. The name "liver-resin" is proposed for it. Liver oil from *Erilepis zonifer* (Lock.) also contains a similar substance (about 4%). These oils and the unsaponifiable matter (especially in carbon disulphide solution) give a deep violet coloration with sulphuric acid. With a sample of *S. ischinagi* liver oil, the coloration was observed to be about one hundred times as strong as that of a cod-liver oil. K. K.

The Highly Unsaturated Acids in Cod-liver Oil. M. Tsujimoto and K. Kimura (*J. Chem. Ind. Japan*, 1923, **26**, 1162).—By the potassium salt–ether method, and the lithium salt–acetone method, a mixture of highly unsaturated acids was obtained. By converting it into the methyl ester, a fraction (about 4% of the oil) boiling at 220—226°/5 mm. was isolated. The analysis of the ester and the fatty acid from the ester gave $C_{22}H_{33}O_2Me$ and $C_{22}H_{34}O_2$ respectively, and behenic acid was produced from the latter by hydrogenation. Cod-liver oil therefore contains a large amount of clupanodonic acid, $C_{22}H_{34}O_2$. The part of the methyl ester boiling below 220°/5 mm. is supposed to contain a large amount of a highly unsaturated acid containing eighteen or twenty carbon atoms. K. K.

Further Studies on Autoxidations and Oxido-reduction Processes. V. E. Abderhalden and E. Wertheimer (*Pflüger's Archiv*, 1923, **200**, 176—193; from *Chem. Zentr.*, 1923, iii, 1290).—The reducing power of muscle in which thermal rigor has been induced is three or four times that of normal muscle. In chemical rigor and rigor mortis, there is a similar increase in reducing power. An increase also occurs during normal or tetanic contraction. It is supposed that such increases are associated with the presence of a thiol group in the muscle fibres. Cysteine serves as a hydrogen carrier and acceptor. A scheme for a stable oxido-reduction system is given. G. W. R.

A Methylation Function of the Thyroids and the Biological Significance of Iodine. B. Stuber, A. Russman, and E. A. Proebsting (*Biochem. Z.*, 1923, **143**, 221—234).—If guanidineacetic acid be administered intravenously to young dogs, an increase of blood creatine–creatinine follows. No such increase occurs in thyroidectomised animals, but if these be given dried thyroid or potassium iodide per os, before the injection of guanidineacetic acid, they react like the normal animals. The blood of normal dogs, but not of thyroidectomised dogs, is also effective in this respect. It is concluded that the capacity of the organism to methylate guanidineacetic acid, and so form creatine and creatinine, is dependent on the integrity of the thyroids, and that iodine compounds are necessary for this methylation process. J. P.

The Oxytocic–Pressor–Diuretic Principle of the Infundibular Portion of the Pituitary Gland. J. J. Abel, C. A. Rouiller, and E. M. K. Geiling (*J. Pharm. exp. Ther.*, 1923, **22**, 289—316).—After a purification of the gland material by precipitation with mercuric chloride, phosphotungstic acid, and tannic acid in succession, the residue is dissolved in an alcoholic solution of tartaric acid and re-precipitated with ether. The resulting precipitate is called the tartrate of the active principle. Its action on the isolated uterus of the guinea-pig may be as much as 1,250 times as great as that of histamine phosphate, whilst it also retains the diuretic and pressor action characteristic of the pituitary extract. C. R. H.

Anaërobic Processes Involved in Muscular Activity. W. Hartree and A. V. Hill (*J. Physiol.*, 1923, **58**, 127—137).—In muscle, 0·1% of lactic acid can be produced so rapidly by exercise or by stimulation that no appreciable escape of carbon dioxide or of acid is possible. Hence if the hydrogen-ion concentration inside a muscle is not to rise to an excessive degree during exercise, there must be some buffer in it, much more effective than a bicarbonate solution. Meyerhof (*Pflüger's Archiv*, 1922, **195**, 22) has emphasised that in a frog's muscle the absolute amount of bicarbonate present, as determined from the carbon dioxide driven out from the muscle by excess of acid, is quite inadequate to neutralise the lactic acid liberated in severe stimulation. Even if all the carbon dioxide were driven out, only one-seventh to one-tenth of the lactic acid could be neutralised.

The authors further calculate that the 0·3% inorganic phosphate in muscle (a mixture of KH_2PO_4 and K_2HPO_4) is also quite inadequate to keep the P_H within the extreme limits observed, viz., a change from 7·5 to 6·9). Bicarbonate and phosphate together are insufficient to neutralise half the lactic acid formed. There must be, as Meyerhof assumes, some other powerful buffer, doubtless an alkali–protein salt. The addition of lactic acid to shed blood also produces only a fraction of the change in the hydrogen-ion, which would result in a bicarbonate solution of the same concentration; here also alkali protein must play a considerable part.

The authors confirm the existence of a secondary maximum in the production of heat in a muscle in the absence of oxygen; this maximum occurs after about two and a half minutes (see the following abstract for its interpretation). A "balance sheet" is given of the heat evolved in the different phases of muscular contraction; it shows that during the recovery process something between 1/4·7 and 1/6 of the lactic acid removed is oxidised, the rest being reconverted into glycogen. G. B.

Heat of Combustion of Glycogen in Relation to Muscular Contraction. W. K. Slater (*J. Physiol.*, 1923, **53**, 163—167).—Glycogen (from *Mytilus edulis*, a convenient source) only becomes anhydrous at 100° in a vacuum over phosphoric oxide (cf. Harden and Young, T., 1902, **81**, 1224). Dried by the method of Atkins and Wilson (T., 1915, **107**, 916), it has the composition $(C_6H_{10}O_5,H_2O)_n$.

The heat of combustion seems previously to have been determined with slightly hydrated material. The author finds the heat of combustion of hydrated glycogen to be 3,883 cal. per gram, which is about 100 cal. higher than that calculated from Stohmann and Schmidt's value, 4,190 (A., 1895, ii, 102), for (presumably imperfectly) dehydrated glycogen, for this would give for the hydrated form 162/180 × 4,190 = 3,771 cal. The heat of wetting is found to be about 9 cal., hence the heat of combustion of hydrated glycogen in solution is 3,874 cal. The heat of combustion of lactic acid is, according to Meyerhof, 3,601 cal., leaving 273 cal. for the conversion of 1 g. of glycogen into 1 g. of lactic acid. The heat of neutralisation of lactic acid by acid salts is, according to Meyerhof (*loc. cit.*), 19 cal. per g., which leads to the value 273 + 19 = 292 cal. for the heat liberated during contraction and relaxation of a muscle, per g. of lactic acid formed. The total initial heat, given by Hartree and Hill in their balance-sheet (as the result of physical measurement, see preceding abstract) is 296 cal., in close agreement with that calculated above. The salt buffering of the lactic acid is, however, probably only of a temporary character and is replaced by the more efficient buffering by alkali-protein. Meyerhof has shown that the neutralisation of 1 g. of lactic acid by alkali-protein produces 138 cal., or 119 more than that by salts. The whole of these 119 cal. are, however, not produced; according to Hartree and Hill the delayed anaërobic heat production is 74 cal. per g. of lactic acid, so that only about 60% of the lactic acid formed is neutralised by alkali protein (the rest remains neutralised by salts). The delayed heat production, presumably due to a transfer of alkali from protein to acid phosphate and carbonic acid, is the cause of the secondary maximum in the heat production occurring after two and a half minutes (preceding abstract). The velocity of this reaction is independent of the temperature, and thus probably depends on a physical process (rate of diffusion of acid phosphate- and carbonic acid-ions) through the muscle-tissue. This theory demands some special distribution of phosphate and carbonate molecules in the muscle substance, and may be represented by the following scheme:

Contraction (*a*) Glycogen ⟶ lactic acid; (*b*) lactic acid and contractile mechanism produce mechanical response.

Relaxation (*a*) Lactic acid + K_2HPO_4 and $KHCO_3 \longrightarrow$ K lactate + KH_2PO_4 and H_2CO_3.

Anaërobic recovery (*a*) KH_2PO_4 and H_2CO_3 + K protein $\longrightarrow$ $K_2HPO_4 + KHCO_3$ + H protein. G. B.

Products of the Catalytic Hydrolysis of Horse Hair. V. S. Sadikov (*Biochem. Z.*, 1923, **143**, 504—511).—Fractionation of the product obtained by the catalytic hydrolysis of horse hair under pressure yielded the following substances: (1) A peptide anhydride (m. p. 258°) of alanine and leucine to which the formula $C_{21}H_{36}O_4N_4$ or $C_{21}H_{38}O_4N_4$ is ascribed. (2) A peptide anhydride of alanine and leucine (m. p. 260°) of the formula $C_9H_{16}O_2N_2$. (3) A peptide anhydride of leucine and valine (m. p. 246°) of the formula

$C_{11}H_{20}O_2N_2$. (4) Butylalanyl-leucine anhydride, $C_{10}H_{18}O_2N_2$, or its unsaturated derivative, $C_{10}H_{16}O_2N_2$ (m. p. 224°). (5) Diketomethylpiperidine, $C_6H_9O_2N$ (m. p. 196°). (6) A cyclic nitrogen substance, $C_{15}H_{30}N$, of an alkaloidal nature. (7) A substance of the formula $C_{13}H_{20}O_3N_2$ (m. p. 170°). Various other less well characterised derivatives of the nature of diketopiperazines and keto- and diketo-piperidines were obtained. J. P.

Calcium Fixation by Animal Tissues. IX. E. FREUDENBERG and P. GYÖRGY (*Biochem. Z.*, 1923, **142**, 407—416).—A study has been made of the extent to which calcium phosphate and carbonate are formed, when solutions of casein and egg-albumin are treated with sodium phosphate or carbonate at different p_H, and dialysed against calcium chloride. After dialysis the distribution of calcium, phosphate, and fixed carbon dioxide was determined both externally and internally, and the bearing of the results on the process of calcification occurring in animal tissues is discussed. The conclusion is drawn that a reversible fixation of calcium by the tissue proteins takes place. With diminishing metabolic activity, the fixed calcium reacts with phosphate and carbonate to give rise to complex protein–calcium–phosphate–carbonate compounds from which the carbonate is gradually eliminated by the acid nature of the proteins under tissue conditions. The excess of calcium phosphate is then split off, leaving the original active group of the protein free to combine with more calcium (cf. also György, this vol., i, 120). J. P.

The Basis of the Oxidation Theory of Wieland. O. WARBURG (*Biochem. Z.*, 1923, **142**, 518—523).—A criticism of Wieland's views on the mechanism of oxidation. In place of the theory that organic oxidations proceed in two phases, first hydration followed by abstraction of hydrogen by interaction with molecular oxygen, the theory advanced by the author supposes that molecular oxygen is first activated by combination with a catalyst (iron, platinum, or organic catalyst) and then reacts directly with the oxidisable substance. It is argued that Methylene-blue, quinone, etc., do not react like molecular oxygen when substituted for the latter (Wieland, A., 1913, i, 1304), but as activated oxygen, *i.e.*, molecular oxygen + catalyst. The action of hydrocyanic acid in inhibiting oxidations is regarded as opposing Wieland's theory, whilst it receives a ready interpretation on the author's views, since it combines with the catalyst (*e.g.*, iron) and prevents the activation of the oxygen. J. P.

Carnisapidine in Animal Tissues. F. BATTELLI and L. STERN (*Compt. rend. Soc. Biol.*, 1923, **88**, 575—577; from *Chem. Zentr.*, 1923, iii, 1037).—The constituent of animal tissues to which the taste is due is named by the author *carnisapidin*. The amount present in different tissues was determined approximately by dilution of extracts until the taste was just perceptible. The highest content was found in muscles, liver, spleen, and kidneys, lower amounts were found in the thymus, brain, and lungs. G. W. R.

Sarcochromogen in Animal Tissues. F. BATTELLI and L. STERN (*Compt. rend. Soc. Biol.*, 1923, **88**, 679—681; from *Chem. Zentr.*, 1923, iii, 1037; cf. preceding abstract).—Aqueous extracts of animal tissues contain a sarcochromogen which differs from sarcochrome in not being precipitated by metaphosphoric acid. Sarcochromogen is not changed into sarcochrome on evaporation to dryness if the temperature remains below 80°. G. W. R.

The Rôle of Carnisapidin and Sarcochromogen in Animal Tissues. L. STERN and F. BATTELLI (*Compt. rend. Soc. Biol.*, 1923, **88**, 681—683; from *Chem. Zentr.*, 1923, iii, 1037; cf. preceding abstracts).—The occurrence of carnisapidin and sarcochromogen in animal tissues appears to have no direct correlation with metabolic exchange. Certain proteins such as casein give, on treatment with pepsin, substances analogous to sarcochromogen. Carnisapidin and sarcochromogen are easily dialysable, and are not attacked by digestive ferments. Carnisapidin, administered intravenously, is eliminated in the urine, but when administered orally or subcutaneously it is retained or decomposed, probably in the liver. G. W. R.

The Extractives of *Actinia equina*. D. ACKERMANN, F. HOLTZ, and H. REINWEIN (*Z. Biol.*, 1924, **80**, 131—136; cf. A., 1923, i, 1155).—The extractives of *Actinia equina* were subjected to fractionation by Kossel and Kutscher's method. The histidine and arginine fractions have not yet been worked up. In the purine fraction there was obtained adenine, isolated in the form of its picrate. From the lysine fraction there was obtained (1) tetramethylammonium hydroxide (as picrate); (2) a base, identified as pyridylmethylammonium hydroxide (*chloroaurate*, m. p. 252—253°, and *chloroplatinate*); (3) a base of unknown constitution, *actinine*, $C_{13}H_{24}O_5N_2$; from it there were prepared a *chloroaurate*, m. p. 169°, a *chloroplatinate*, dark red, crystalline nodules, decomp. 209°, and a *hydrochloride*, m. p. 207—208°. C. R. H.

The Chemical Differential Diagnosis of Transudates and Exudates. K. HIRUMA (*Biochem. Z.*, 1923, **142**, 506—517).—Exudates contain an albumin precipitable by an acetate mixture at C_H $0{\cdot}36 \times 10^{-4}$, by a phosphate mixture at C_H $0{\cdot}214 \times 10^{-2}$, and by a citrate mixture at C_H $1{\cdot}13 \times 10^{-4}$. Inflammatory cerebrospinal fluids contain the same type of albumin as the exudates formed in pleurisy and in peritonitis. The average sugar content of transudates is 0·115% and of exudates 0·07%, the former being in general above the plasma sugar value of the patient, and the latter somewhat lower. The residual nitrogen of transudates, and the amino-nitrogen and ammonia of both transudates and exudates, are approximately the same as those of the blood, whilst the residual nitrogen of exudates is higher than that of transudates. In nephritis, the residual nitrogen is greater the more marked is the œdematous condition. J. P.

The Distribution of Nitrogen in the Urine of Young Dogs and its Dependence on Diet. F. SERIO (*Biochem. Z.*, 1923, **142**, 440—453).—The distribution of nitrogen in the urine of young dogs kept on a diet rich in fat but poor in, or free from, nitrogen is similar to that of starved animals. The urea is diminished and the ammonia increased due to starvation acidosis. The excretion of amino-acids is not influenced by a low nitrogen diet, but it is lowered on a milk diet. The " urease " method for estimating urea gives lower results than the Mörner-Sjöquist method, a difference which is more marked the smaller the ratio of urea nitrogen to total nitrogen becomes. During the period of pre-mortal increase in the nitrogen excretion, the difference disappears, and it is less apparent on a milk diet. The suggestion is made that the difference is due to allantoin and creatinine being estimated along with urea in the Mörner-Sjöquist method, and that the excretion of these urinary constituents varies under the conditions studied, ceasing during the pre-mortal period. J. P.

Sulphatase. III. The Enzymatic Fission of the Ethereal Sulphates in the Urine of the Horse, Camel, and Dog. J. Noguchi (*Biochem. Z.*, 1923, **143**, 186—189).—By treating horse and camel urine with preparations of sulphatase at 37°, hydrolysis of the ethereal sulphates varying from 60 to 90% was obtained. Similar extensive hydrolysis of the organic sulphates occurred in the urine of a dog to which phenol had been administered. J. P.

Acetonuria and Acidosis. D. Adlersberg (*Biochem. Z.*, 1923, **143**, 527—532).—From a study of the effect of orally administered ammonium dihydrogen phosphate on normal subjects kept on a diet free from carbohydrate, and on diabetic subjects, it is concluded that acidosis diminishes the urinary excretion of ketone substances in these conditions. J. P.

Thymolglycuronic Acid. K. Takao (*Z. physiol. Chem.*, 1923, **131**, 304—306).—According to Blum (A., 1892, 1116), thymol is not excreted by the dog as thymolglycuronic acid, although it is so in man. It is now shown, however, that a very small fraction of it is so excreted by the dog. By treatment with sodium hypochlorite and fuming hydrochloric acid, thymolglycuronic acid in the urine was converted into *dichlorothymolglycuronic acid*, $C_{16}H_{22}O_8Cl_2$, colourless needles, m. p. 118—119°, $[\alpha]_D^{20}-66{\cdot}46°$ ($c = 3{\cdot}9497\%$) (*barium* salt, $[C_{16}H_{21}O_8Cl_2]_2Ba$). W. O. K.

Phosphorus Metabolism in Avitaminosis. K. Morinaka (*Biochem. Z.*, 1923, **142**, 381—384).—The phosphorus content of the livers of avitaminosed rats to which sodium phosphate, lecithin, or phosphoprotein has been administered does not differ appreciably from that of the livers of similarly fed normal rats. The conclusion is drawn that in avitaminosis the soft tissues do not lose their power of phosphorus retention. J. P.

The Kephalin and Lecithin Content of the Brain in Avitaminosis. H. Naito (*Biochem. Z.*, 1923, **142**, 385—392).—The percentage content of kephalin and lecithin in the brains of avitaminosed rats and guinea-pigs does not depart appreciably from normal, although there is a diminution in the total mass of brain-tissue. J. P.

The Lecithin Content of the Brain and Liver of Normal and Avitaminosed Pigeons after Forced Lecithin Feeding. H. Naito (*Biochem. Z.*, 1923, **142**, 393—397).—Lecithin feeding slightly increases the amount of the lipoid found in the livers of normal, but not in the livers of avitaminosed pigeons. The lecithin of the brain is not affected in either case. It is concluded that in the avitaminosed liver, phosphorus compounds other than lecithin increase at the expense of the latter (cf. Morinaka, above). J. P.

Fat Metabolism in Avitaminosis. IV. The Gaseous Metabolism of Starved Avitaminosed Rats during Digestion and after Adrenaline Injection. K. Asada (*Biochem. Z.*, 1923, **143**, 387—398).—The oxygen consumption of partly and completely avitaminosed rats is sub-normal, both during a period of starvation and while a vitamin-free meal is being digested. The extent of the increase observed under the latter conditions compared with the requirements of the starved animals varies inversely with the severity of the avitaminosis. Adrenaline injections produce a greater increase in oxygen consumption in avitaminosed than in normal rats. A discussion is appended of the earlier results obtained in the study of carbohydrate and fat metabolism in avitaminosis. J. P.

Uric Acid and Allantoin Metabolism in Avitaminosis. A. Adachi (*Biochem. Z.*, 1923, **143**, 408—422).—In avitaminosis, the excretion of allantoin in dogs shows no notable variations, whilst that of uric acid is variable and may show transitory increases. In long-continued avitaminosis, the uric acid excretion is markedly increased and may reach values three times those obtained in normal animals. It is concluded that an increased consumption of nucleins occurs in the later stages of avitaminosis. J. P.

The Pharmacology of the Rare Earths. I. Cerium. S. Hara (*Arch. expt. Path. Pharm.*, 1923, **100**, 217—253).—In general, cerium bears a close resemblance to aluminium and to the heavy metals in its pharmacological action. Proteins are precipitated by moderate but not by strong concentrations of its salts. C. R. H.

The Pharmacology and Toxicology of Carbon Tetrachloride. P. D. Lamson, G. H. Gardner, R. K. Gustafson, E. D. Maire, A. J. McLean, and H. S. Wells (*J. Pharm. expt. Ther.*, 1923, **22**, 215—288).—A comprehensive study of the pathological effects following administration to dogs of carefully purified carbon tetrachloride. Oral administration produced only slight and transitory symptoms unless accompanied or preceded by administration of fats or alcohol. When given intravenously, it is lethal in doses of 0·154 c.c. per kg. body-weight.

The pathology of carbon tetrachloride poisoning consists essentially (apart from local irritant effects such as bronchitis following inhalation) in damage done to the liver, one of the first indications of which is the appearance of abnormal amounts of bilirubin in the blood. C. R. H.

The Rôle of certain Carbohydrates in the Organism. E. O. FOLKMAR (*Bibliotek laeger*, 1923, **115**, 120—125; from *Chem. Zentr.*, 1923, iii, 1291).—With continued intravenous injection of pentoses in small amounts at a rate comparable to intestinal absorption, approximately one-half is excreted in the urine. Galactose can be assimilated at the daily rate of 1—2 g. per kg. of live weight without glycosuria or appreciable increase in blood-sugar. Maltose is well utilised, after becoming hydrolysed by maltase. There is an appreciable retention of sucrose in certain circumstances; invertase is, however, not present in blood. Raffinose is completely excreted. The small amounts of ethyl alcohol normally present in blood are attributed to casual decomposition of carbohydrates and not to the action of an alcoholase. G. W. R.

The Influence of Oral Administration of Dextrose on the Blood-sugar and on Glycosuria in Healthy Individuals. G. CONSTAM (*Biochem. Z.*, 1923, **143**, 75—104).—The elimination of sugar in the urine is best followed by estimating the amount excreted in unit time. Observations based purely on changes in concentration do not give dependable results. In normal individuals a mixed meal is followed by a definite glycosuria. Tap water produces a dilution glycosuria which reaches a maximum in about one hour. The assimilation limit for sugar in the same individual is variable and is higher after five hours' than after fourteen hours' abstention from food, whilst the assimilation capacity varies in the opposite sense. In the cases quoted, the tolerance lay between 100 and 150 g. of dextrose in 500 c.c. of water after five hours, and between 20 and 30 g. in the same volume after fourteen hours' starvation; less concentrated solutions caused dilution glycosuria which diminished with increasing concentration of dextrose until the assimilation limit was reached, when a true glycosuria supervened. The blood-sugar reaches its maximum about half an hour before the urinary sugar. The suggestion is made that the power of the organism to raise the sugar tolerance is a protective mechanism which prevents loss of sugar during periods of diminished rate of assimilation. J. P.

A New Method of Preparing *s*-Diphenylguanidine. Its Pharmacological Effects. O. RIESSER (*Z. physiol. Chem.*, 1923, **131**, 204—213).—Diphenylguanidine is formed together with a small amount of triphenylmelamine when dicyanodiamine is heated with aniline hydrochloride at 190—200°. It crystallises from alcohol in white needles, m. p. 145—148°, and forms a chloroaurate. The pharmacological action of this substance has been investigated. It increases the reflex irritability and also causes central paralysis. In warm-blooded animals, it causes death by arrest of the respiration. It produces progressive paralysis when applied to isolated frog's muscle. W. O. K.

Chemistry of Vegetable Physiology and Agriculture.

Biology of *Bacillus coli communis*. Attempts at "Dysmutation." O. Fernández and T. Garmendia (*Anal. Fis. Quim.*, 1923, **21**, 481—492).—A study of the effect of various reagents on the fermentation of dextrose by *B. coli communis*. Dysmutation consists in the formation of alcohol, acetic acid, and glycerol from sugars through the acetaldehyde formed as an intermediate stage undergoing the Cannizzaro reaction yielding ethyl alcohol and acetic acid. The dysmutation effect, as judged by the amount of acetic acid produced from dextrose was considerable in the case of cultures to which sodium hydrogen carbonate was added. Less appreciable effects were produced where amino-acids were added. G. W. R.

The Decomposition of *d*-Glucosamine by Micro-organisms. K. Takao (*Z. physiol. Chem.*, 1923, **131**, 307—318).—*Bacillus subtilis*, grown on a synthetic medium, with or without the addition of peptone, in presence of *d*-glucosamine forms from the latter succinic acid and a small quantity of lactic acid. If a modified medium is used in which no carbonate is present, lactic acid, but no succinic acid is formed. *B. coli* also forms lactic acid and succinic acid, whilst *B. prodigiosus* forms only lactic acid when grown on a synthetic medium containing *d*-glucosamine. W. O. K.

The Sulphur Cycle in Soil. (The Biology of Thiosulphate Bacteria.) G. Klein and A. Limberger (*Biochem. Z.*, 1923, **143**, 473—483).—The thiosulphate bacteria present in soil can be cultured aërobically in inorganic or organic media, and are capable of oxidising the various inorganic compounds of sulphur which occur in soils to sulphuric or polythionic acids. They also oxidise the sulphur of cystine, and to a less extent that of albumin and nuclein to sulphuric acid. Sulphur is an intermediate product in all cases and may separate in a crystalline condition. In the presence of potassium nitrate, the oxidation is accompanied by the formation of nitrite and ammonia, whilst the presence of ammonium chloride gives rise to the former. The spores of the bacteria are found in water and air as well as in the soil. Considerable importance is attached to the part played by these bacteria in the sulphur cycle occurring between the plants and animals. J. P.

The Influence of Oxygen on the Assimilatory and Dissimilatory Activity of Yeast. III. The Behaviour of Added Alcohol in a Yeast Suspension. H. Lundin (*Biochem. Z.*, 1923, **142**, 454—462).—Arising from the author's previous work (A., 1923, i, 1268), a study has been made of the capacity of aqueous yeast suspensions, containing no carbohydrate or source of nitrogen, to assimilate added ethyl alcohol both under normal conditions and in the presence of excess of oxygen. In contrast to the results

obtained with "nascent" alcohol formed from carbohydrate which is assimilated both with and without excess of oxygen, added alcohol is only assimilated when a stream of oxygen is passed through the solution. Carbohydrate alone is formed and the yeast-cells increase in mass, but not in numbers. On the assumption that no direct oxidation of part of the added alcohol occurs (*loc. cit.*), it is shown that a utilisation of a portion of the assimilated carbohydrate takes place which runs parallel with its formation. A summary is given of the present results, together with the author's earlier observations.
J. P.

The Influence of Oxygen on the Assimilatory and Dissimilatory Activity of Yeast. IV. The Behaviour of certain Organic Acids. H. Lundin (*Biochem. Z.*, 1923, **142**, 463—492).—The methods already described (cf. preceding abstract) have been extended to a study of the capacity of a yeast suspension to assimilate various organic acids. The sodium and ammonium salts of citric, malic, tartaric, and succinic acids are not assimilated even in the presence of an excess of oxygen, and the added salts are without influence on the course of self-fermentation of the yeast. Potassium acetoacetate is assimilated more especially in concentrations of about 1%. Potassium carbonate is formed at the same time, and unless the p_H is adjusted the process is arrested. It is supposed that acetone and carbon dioxide are formed, and the former, in the nascent state, is assimilated to form carbohydrate when an excess of oxygen is provided. The newly-formed carbohydrate may then undergo oxidation. As in the previous experiments, carbohydrate alone is formed, and no alteration in the protein constituents of the yeast is noted. J. P.

Carboligase. VI. A New Type of Change of Acetaldehyde by Fermenting Yeast. C. Neuberg and E. Reinfurth (*Biochem. Z.*, 1923, **143**, 553—565).—The addition of acetaldehyde to dextrose, lævulose, or sucrose undergoing fermentation by top- or bottom-yeasts, leads to the formation of optically active acetylmethylcarbinol, $CH_3\cdot CH(OH)\cdot CO\cdot CH_3$. This "acyloin" synthesis also occurs in cell-free fermentations. Part of the acetaldehyde undergoing condensation arises from the sugar (cf. A., 1923, i, 973).
J. P.

The Fermentation Co-enzyme (Co-zymase) of Yeast. I. H. v. Euler and K. Myrbäck (*Z. physiol. Chem.*, 1923, **131**, 179—203).—Yeast was obtained free from co-enzyme by grinding up the dry yeast with water, centrifuging, again grinding up with water, and centrifuging. The product was then diluted to a given volume with water. A solution of co-enzyme was obtained by boiling yeast with water for a few minutes and if necessary filtering. The co-enzyme is completely precipitated by 50—80% alcohol.

The effect of variation of the p_H on the rate of fermentation of dextrose by various yeasts has been investigated (cf. Euler and Heintze, A., 1920, i, 513). Fermentation is most rapid at p_H 6·2—6·8. Fresh yeast preserves its maximum fermentation over a greater range of p_H than dried yeast. For autofermentation, the optimum p_H is 5—6. The observation of Harden that the activity is very dependent on the amount of phosphate-ion present is confirmed. The activity is a maximum at a certain optimum phosphate content. If there is a constant amount of washed yeast present, then the activity is at first approximately proportional to the amount of the co-enzyme present, and gradually, with increasing co-enzyme, becomes less than required by this relation, and ultimately is approximately constant. Similarly, if the co-enzyme is constant, the activity is at first approximately proportional to the amount of washed yeast, but with large amounts of washed yeast ultimately constant. In presence of constant quantities of washed yeast and of activator, the fermentation increases with increase in the amount of dextrose present to a maximum, and it then decreases. In the absence of phosphate, arsenate does not cause marked fermentation. The co-enzyme is apparently stable in aqueous solution for at least twenty-three hours, and is dialysable through a collodion membrane. It is precipitable by lead acetate and it is not identical with vitamine-*D* as it is not contained in orange juice or malt extract.

W. O. K.

Is Lactic Acid Produced in Alcoholic Fermentation? A. FERNBACH and M. SCHOEN (*Compt. rend. Soc. Biol.*, 1923, **89**, 475—477; from *Chem. Zentr.*, 1923, iii, 1035).—From the products of the alcoholic fermentation of sucrose in the presence of calcium carbonate, *d*- and *l*-lactic acid were isolated as the zinc salts. The *d*-lactate was in excess.

G. W. R.

Formation of Organic Acids by *Sterigmatocystis nigra* [*Aspergillus niger*] in Unbalanced Media. M. MOLLIARD (*Compt. rend.*, 1924, **178**, 41—45).—Previous work (A., 1922, i, 611) is continued from a more quantitative point of view. Known weights of the fungus were allowed to grow in presence of media of different composition (varying the proportions of sucrose and inorganic salts), and the amounts of citric and gluconic acid produced determined from time to time. It is shown that reduction of the proportion of nitrogen present favours the production of gluconic acid, reduction of the other inorganic constituents of the culture medium (phosphorus, potassium, magnesium, iron, and zinc) causing the formation of oxalic and citric acids.

E. E. T.

Antiseptic Action of the Zinc Chloride Salt of Aniline. J. W. HOWARD and F. D. STIMPERT (*J. Amer. Chem. Soc.*, 1923, **45**, 3106—3108; cf. A., 1899, i, 40; 1911, i, 191; 1912, i, 363).—The salt $(NH_2Ph)_2,ZnCl_2$ was formed by intimately mixing aniline and fused zinc chloride; it melts at 255°, and is soluble to the extent of 0·64 g. in 100 c.c. of water at 20°, 0·87 g. in 100 c.c. of 0·4% hydrochloric acid at 20°, and 0·066 g. in 100 c.c. of 95% alcohol at 20°. It is readily decomposed by *N* sodium hydroxide or boiling water. Tests with a culture of *Staphylococcus aureus* indicate that the salt has greater bactericidal action than either aniline or zinc chloride, the respective relative efficiency being approximately 10 : 7½ : 2.

F. B.

The Evolution of Phosphorus during Germination. M. H. VAN LAER and R. DUVINAGE (*Bull. Soc. chim. Belg.*, 1923, **32**, 355—357).—Determinations of the amount of phosphorus and its distribution in the various parts of the grain have been carried out in the case of barley, the grains themselves, the straw, endosperm, seeds, and roots being examined. The grains were first soaked and then allowed to germinate at 15°. The following facts were established: (1) soaking involves an elimination of about 10% of phosphorus; this takes effect both on the straw and on the endosperm; (2) during germination, a migration of phosphorus from the endosperm to the embryo occurs; (3) kilning of the grain has little effect. In the raw barley, the embryo is rich in phosphorus whilst the straw is poor; during germination the phosphorus content of the endosperm diminishes. It is shown that in the embryo, although the amount of phosphorus is greatly increased, the percentage amount remains practically constant, owing to the development of the embryo itself. During germination, a portion of the phosphorus is rendered soluble, and it is this soluble phosphorus which migrates to the embryo. F. G. P.

Theory of Carbonic Acid Assimilation. WO. OSTWALD (*Kolloid Z.*, 1923, **33**, 356—368).—A theoretical paper in which the experimental work on this subject is briefly summarised and the points are noted which must be covered by any theory of assimilation. The following new hypothesis is developed. The primary process of assimilation is a photo-autoxidation, which consists in the formation of a lipoid peroxide sparingly soluble in water. The second process is the formation of an additive compound of albumin and carbon dioxide; this is followed by the interaction of the lipoid peroxide and the albumin–carbon dioxide complex with water in which oxygen is given up, whereby, either, according to Wislicenus's reaction, carbonate is reduced by hydrogen peroxide, or through the formation of an albumin–carbon peroxide compound the reduction through formic acid to formaldehyde takes place. The fourth process consists in the recombination of an oxygen atom with the lipoid oxide to re-form the lipoid peroxide. This combination takes place in the presence of light in chlorophyll-bearing cells and brings the system back to its initial condition. The lipoid peroxide appears to be the "photochemical motor" of the assimilation process. The photochemical reaction in assimilation is not a photo-reduction, but a photo-autoxidation. The whole of the reactions take place in the interface albumin–lipoid, and all work in such a way that the interface is maintained. Chlorophyll appears not to take part in the assimilation process; stoicheiometrically its action probably consists in a physico-chemical promotion of the photo-autoxidation of the lipoid. J. F. S.

Composition of Vegetable Juices obtained by Pressure. G. ANDRÉ (*Compt. rend.*, 1924, **178**, 114—116).—Previously (*ibid.*, 1922, **175**, 286) it was shown that when certain fruit juices are filtered through porous porcelain impregnated with collodion, inorganic, but not organic, phosphorus passed through, whilst the fraction of the total nitrogen passing through was of the same order as the fraction not coagulable by heating at 100°. The relative proportions of filtrable, coagulable, and total nitrogen remain almost constant during growth in the case of potatoes; with increase of filtration pressure, the ratio inorganic phosphorus : total phosphorus increases, that of total phosphorus to total nitrogen remaining constant. E. E. T

Wood Sap. I. Presence of Enzymes in Wood Sap. II. Variations in the Amount of Oxydases in Wood Sap during the Bleeding Period. E. PH. VOTCHAL (*Pamphlet*, Moscow, 1916).—The sap in the outer annual rings in healthy trees is completely sterile. Oxydases and diastases are shown to be present. The maximum oxydase content is reached when trees break into leaf. G. W. R.

The Anthocyans in Norton and Concord Grapes. The Chemistry of Grape Pigments. R. J. ANDERSON (*J. Biol. Chem.*, 1923, **57**, 795—813).—The pigments present in two varieties of American grapes, namely, Norton (*Vitis æstivalis*, *V. labrusca*) and Concord (*V. labrusca*), have been examined by the methods of Willstätter and Zollinger (A., 1915, i, 285; 1917, i, 47). The same anthocyanin chloride, $C_{23}H_{25}O_{12}Cl,3H_2O$, has been isolated from both varieties. On hydrolysis, it yields dextrose and an anthocyanidin chloride, $C_{17}H_{15}O_7Cl,1\frac{1}{2}H_2O$. The substances are identical in composition with the oenin and oenidin chlorides obtained by Willstätter and Zollinger from European grapes (*V. vinifera*), but they differ from these substances in that the anthocyanidin contains only one methoxyl group, whereas oenidin contains two. The colour reactions are, moreover, different. The anthocyanin gives with ferric chloride in aqueous solution a purple colour which quickly fades to light brown, and in alcoholic solution an intense blue which changes to purple and finally to wine-red; the anthocyanidin gives with the same reagent both in aqueous and alcoholic solution a momentary purple colour fading to an almost colourless or faintly yellow solution. Evidence of the presence of a diglucoside has also been obtained. E. S.

Constituents of *Milletia taiwaniana*, Hayata. T. KARIYONE, K. ATSUMI, and M. SHIMADA (*J. Pharm. Soc. Japan*, 1923, No. **500**, 739—746).—Nagai (*J. Tokyo Chem. Soc.*, 1902, **23**, 744) isolated rotenone as one of the poisonous constituents of *Milletia taiwaniana*, Hayata, produced in Formosa. Later, Ishikawa (A., 1918, i, 94) isolated anhydroderride from the mother-liquor of rotenone and pointed out that rotenone was not identical with tubotoxin, a poisonous constituent of *Derris elliptica* (*J. Pharm. Soc. Japan*, 1923, No. **491**, 10). The authors have established the identity of rotenone and tubotoxin from the coincidence of the following properties: Crystalline forms (rhombic plates from hot alcohol or needles from benzene); m. p. 163°; (mixed sample gave the same m. p.), empirical formula, $C_{18}H_{18}O_5$, $[\alpha]_D^{20}$ $-236\cdot5°$ to $-244°$, oxime,

m. p. 245°, and phenylhydrazone, m. p. 255°. The authors have retained the name rotenone, as it was the first proposed. From crude rotenone, a white, wax-like, amorphous substance was isolated; it has m. p. 80°, acid value 15·85, saponification value 33·92 (118·70 after acetylation), and iodine number 17·02. K. K.

The Acids and Red Colouring Matter of the Horned Poppy (*Glaucium luteum*). H. Schmalfuss (*Z. physiol. Chem.*, 1923, **131**, 166—167).—The following acids have been obtained from the juice expressed from the horned poppy: citric acid, 25·82%, lactic acid, 18·24%, acetic acid, 11·88%, succinic acid, 1·99%, fumaric acid, 21·59%, malic acid, 13·50%, anhydromalic acid, 5·92%, βγ-dihydroxy-Δ^{β}-butene-αδ-dicarboxylic acid, 1·07%, the steric configuration of which has not been determined, and traces of formic acid. The hydrochloric acid extract of the pulp left contained fumaric acid 34·33%, malic acid 12·53%, and oxalic acid 53·14%. No trace of maleic acid could be detected in the plant. The red colouring matter appears to be a lipochrome. W. O. K.

Lipase in Sunflower (*Helianthus annuus*) Seeds. F. Traetta-Mosca and F. Milletti (*Ann. Chim. Applicata*, 1923, **13**, 270—288).—The authors give a summary of the literature dealing with the lipolytic enzymes of seeds and describe experiments which show that sunflower seeds exhibit lipolytic activity, this being only slight in the quiescent seeds, but becoming more intense in germinating and also in de-fatted seeds. Experiments with oleic acid and glycerol yield results showing that the lipase of sunflower seeds exerts also a synthetic action. Acid is liberated in gradually increasing proportions from linseed, cotton-seed, and castor oils by the agency of sunflower seeds. T. H. P.

Phosphate Behaviour in Soils. J. S. Burd and J. C. Martin (*Science*, 1923, **58**, 227—228).—By use of the authors' method (*J. Agr. Sci.*, 1923, **13**, 265) for the extraction of what is probably the true soil solution, it has been shown that after a volume of solution equal to the amount of water initially contained in the compacted soil has been removed, the solutions obtained from a second displacement of the same mass of soil with an equal amount of water have decreasing total concentrations of electrolytes, but the phosphate concentrations increase. Thus, at the approach of the end of the growing season, the diminished total concentration in the soil solution is probably accompanied by a tendency towards enhancement of the concentration of phosphate. An apparent result of this effect has been observed, although it may easily become masked by experimental error in soils of low total concentration or by increased absorption of phosphate by the plant in the later stages of growth. A. A. E.

Organic Chemistry.

The Combustion of Methane to Formaldehyde. H. TROPSCH and O. ROELEN (*Brennstoff-Chem.*, 1924, **5**, 37—42).—A gas mixture containing methane and oxygen was passed through a quartz tube (without a catalyst), heated in an oven, and the formaldehyde produced absorbed in water and determined titrimetrically. The effect of varying the methane : oxygen ratio in the gas, the diameter of the tube, the reaction temperature, and the gas velocity through the tube, was studied. The yield of formaldehyde first increases with increasing gas velocity (the other factors being kept constant), reaches a maximum, and then decreases, a characteristic curve being obtained by plotting the results graphically. In the experiment in which the highest yield of formaldehyde was obtained the gas velocity was as high as 20 m. per sec. The tubes employed had cross-sectional areas of 63·5, 13·5, and 1·4 sq. mm., respectively, and the highest yields were obtained with the second of the three. If the oxygen content of the gas used is maintained constant (about 16—19%) and the methane content is varied, the highest concentration of formaldehyde in the resulting gas is obtained with a methane : oxygen ratio of 1 : 1, as required by theory. When working at high temperatures, the maximum is only obtained by starting with a high gas velocity and gradually diminishing it, much lower results being obtained by working conversely. With increasing reaction temperature, the absolute quantity of formaldehyde produced increases, but the yield per unit of methane decomposed diminishes. The highest yield of formaldehyde, viz., 5·96% of the methane treated, was obtained with a gas containing 1·2% of methane and 19·4% of oxygen, whilst a maximum yield of 70% of the methane decomposed was obtained at a reaction temperature of 700°, showing that formaldehyde is formed as the principal product in the action of oxygen on methane. Discrepancies between the present results and those of previous workers are discussed. W. T. K. B.

The Influence of some Non-inflammable Vapours of Organic Liquids on the Limits of Inflammability of Mixtures of Methane and Air. W. P. JORISSEN and J. VELÍŠEK (*Rec. trav. chim.*, 1924, **43**, 80—86).—The limits of inflammability of mixtures of methane and air are found to be 5·4% and 14·1% of methane. These limits are considerably modified by the presence of vapours of non-inflammable liquids. In presence of 0·7 to 0·8% of perchloroethylene, the limits are 7·35 and 10·15%; with 0·7 to 0·8% of tetrachloroethane, 7·15 and 9·15%; with 1% of pentachloroethane, 5·95 and 10·3%. In presence of 20% of dichloroethylene, 5% of trichloroethylene, or of 12·2% of carbon tetrachloride explosion is entirely inhibited, whilst with 8·5% of carbon tetrachloride the limits are 9·0 and 9·9% of methane.

E. H. R.

The Cracking Process of Burton. H. I. WATERMAN and H. J. W. REUS (*Rec. trav. chim.*, 1924, **43**, 87—92).—It has been claimed that condensation under pressure in the oil-cracking process leads to the production of distillates free from unsaturated hydrocarbons. The authors are unable to verify this claim. [Cf. *B.*, 1924, 207.] E. H. R.

The Generation of Ethylene from Alcohol. T. HISAMURA and Y. IMAOKA (*Kwaken Hôkoku*, 1923, No. 7, 1—21).—Ethylene is prepared by passing alcohol vapour over "adsol" electrically heated at 390—400°, the yield being about 83%. (Adsol is a product used for drying air and is prepared from Japanese acid clay by pressing and burning; cf. Japan. Pat. 42368.) The rate of passing alcohol is 60—80 c.c. (in liquid) per hour, the thickness of the layer of the catalyst is 7 cm., and the resulting gas contains 98% of ethylene. After ten hours' passage of the vapour the yield decreases to 71%; the catalyst may, however, be re-activated by heating it for about thirty minutes at 650—700° in a current of air. K. K.

The Additive Power of Iodine with regard to Ethylenic Compounds. E. ANDRÉ (*Bull. Soc. chim.*, 1923, **33**, [iv], 1641—1647).—The author has studied the action of iodine in various solvents on olive, sesamé, poppy, and cod-liver oils, also on *iso*heptene and phenylbutylene. The results obtained are compared with the iodine values furnished by Hanus' method, and show that the element itself is fairly active. Least activity is shown by the violet solutions in carbon tetrachloride and carbon disulphide; the brown solution in acetic acid and the violet-red chloroform solution exhibit much greater activity, the latter in some cases fixing 97% of the amount used in an iodine value determination. A second series of experiments, in which the iodine concentration was in each case $N/10$, gave similar results from the comparative point of view, although the ratio of iodine fixed to iodine value decreases considerably on dilution. The additive action in respect of ethylenic compounds seems to be capricious, as the same reactants under apparently similar conditions yielded discordant results in many cases. H. J. E.

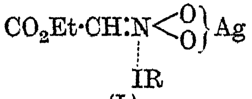
Aliphatic Nitro-compounds. XIV. The Preparation of Nitroacetic Esters and the Alkylation of their Silver Salts. W. STEINKOPF [and, in part, E. A. HAUGEN, A. SCHKADE, T. HÖPNER, and B. NOWY] (*Annalen*, 1923, **434**, 21—34).—Ethyl nitroacetate, b. p. 97°/13 mm., is prepared by passing dry hydrogen chloride into a solution of the acid, or a suspension of its potassium salt, in absolute alcohol at 0°, or by the gradual addition of concentrated sulphuric acid to a solution of the acid in alcohol at —15°. Its ammonium salt, long needles, has m. p. 124° (cf. Bouveault and Wahl, A., 1901, i, 4). The silver salt, if prepared from the pure ammonium salt, may be kept for a week before it becomes discoloured; it darkens at 40°, and decomposes at 117—119°. The following esters are similarly prepared: methyl, b. p. 106—110°/31 mm.; *propyl*, b. p. 105°/18 mm.; iso*propyl*, b. p. 92·2—

93·2°/12 mm. (*ammonium* salt, m. p. 107—109°); iso*butyl*, b. p. 111·5—112·5°/15 mm. (*ammonium* salt, m. p. 110—112°); iso*amyl*, b. p. 122—123°/16 mm. (*ammonium* salt, m. p. 112—115°).

The silver salt of ethyl nitroacetate (1 mol.) is gradually added to methyl iodide (2 mols.) at or below 0°. The product contains ethyl α-nitropropionate (cf. Steinkopf and Supan, A., 1911, i, 4) and *ethyl nitroacetate* aci*methyl ether*, $CO_2Et\cdot CH{:}NO_2Me$, a colourless liquid, b. p. 84°/2·5 mm., which gives a red coloration with ferric chloride, and is decomposed by means of concentrated hydrochloric acid at 70° into formaldehyde and *iso*nitrosoacetic acid. Similarly, the use of ethyl iodide leads to the formation of ethyl α-nitrobutyrate (cf. Schmidt and Widmann, A., 1909, i, 453) and *ethyl nitroacetate* aci*ethyl ether*, a colourless liquid, b. p. 81°/3 mm. These *aci*nitroethers, in which, in addition to the nitro group, there is only one other negative radical, are quite stable, and do not show any tendency to undergo isomerisation to the *C*-alkyl derivative. The view of Hantzsch and Voigt (A., 1912, i, 151), that two such radicals are necessary to stabilise an *aci*nitroether, is therefore incorrect.

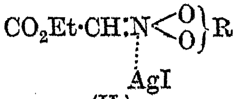
It is probable that the compound, m. p. 114°, obtained by Ratz (A., 1906, i, 238) from silver nitroacetamide and ethyl iodide is an *aci*nitroether of the formula $CH_2ON\cdot CH{:}NO_2Et$.

During the action of methyl iodide on silver ethyl nitroacetate (above), the following phenomena are observed. If the salt is added at about −20°, it dissolves immediately to give a deep brown solution, the colour of which rapidly gives place to a white opalescence; silver iodide is then precipitated. If the addition is made at −60°, there is no reaction; as the mixture is allowed to become warm the solid is gradually dissolved, to give a colourless solution. This is stable over quite a wide range of temperature. Suddenly, however, the solution becomes dark. The brown colour then disappears as before, and silver iodide makes its appearance. It is supposed that in the colourless solution there is a molecular



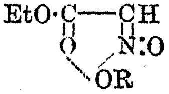
$$\underset{\vdots\atop \mathrm{IR}}{\mathrm{CO_2Et\cdot CH{:}N}}\!\left<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\mathrm{Ag}$$

(I.)



$$\underset{\vdots\atop \mathrm{AgI}}{\mathrm{CO_2Et\cdot CH{:}N}}\!\left<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}\mathrm{R}$$

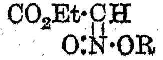
(II.)



$$\begin{array}{lcl}\mathrm{EtO\cdot C} & \text{——} & \mathrm{CH}\\ \quad\| & & \;\|\\ \quad\mathrm{O} & & \mathrm{N{:}O}\\ & \diagdown\;\diagup & \\ & \mathrm{OR} & \end{array}$$

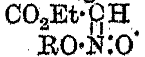
(III.)

compound (I); the appearance of the brown coloration is due to a kind of double decomposition, resulting in the formation of a halochromic complex (II), from which the removal of silver iodide gives stereoisomeric *aci*nitroethers,



$$\begin{matrix}\mathrm{CO_2Et\cdot CH}\\ \quad\;\;\|\\ \quad\mathrm{O{:}N\cdot OR}\end{matrix}$$

and



$$\begin{matrix}\mathrm{CO_2Et\cdot CH}\\ \quad\;\;\|\\ \quad\mathrm{RO\cdot N{:}O}\end{matrix}$$

These are then stabilised, the former by isomerisation to the *C*-alkyl derivative, and the latter by "conjugation" (III) (Hantzsch and Voigt, *loc. cit.*).

iso*Propyl mercuri*aci-*nitroacetate anhydride*, $CO_2Pr^{\beta}\cdot C{<}^{NO}_{Hg}{>}O$, is obtained by the addition of concentrated mercuric chloride solution to an aqueous solution containing sodium acetate and the *aci*ammonium salt of *iso*propyl nitroacetate; the iso*butyl* and iso*amyl* derivatives are prepared in a similar manner. These compounds resemble ethyl nitroacetate *aci*mercurianhydride (cf. Prager, A., 1913, i, 5); they are white solids, which sublime when heated, and are soluble in dilute sodium hydroxide solution, potassium cyanide solution, or hydrochloric acid. The solution in alkali does not react with potassium iodide. The action of mercuric chloride on potassium or ammonium nitroacetate gives, apparently, a heterogeneous product, which does not sublime on being heated, but decomposes violently.

Diammonium nitroacetate, $NH_4O{\cdot}CO{\cdot}CH{:}NO_2{\cdot}NH_4$, a white solid, is obtained from ammonia and nitroacetic acid in dry ethereal solution; the *disilver* salt is also prepared.

Condensation could not be effected between ethyl nitroacetate and benzaldehyde, piperonal, or anisaldehyde, using methylamine, ethylamine, amylamine, or piperidine as catalysts. W. S. N.

The Formation of Ethyl Chloride from Ethylene and Hydrogen Chloride. E. Berl and J. Bitter (*Ber.*, 1924, **57**, [*B*], 95—99).—The union of ethylene with hydrogen chloride in the presence of aluminium chloride is effected most advantageously at 130—170°, but the slowness of the reaction renders prolonged contact with the catalyst necessary for the production of good yields of ethyl chloride; the latter substance is absorbed from the products of the reaction by active charcoal.

Ethyl chloride is analysed by passing it through a very narrow quartz tube heated at 900°, absorption of the hydrogen chloride by sodium hydroxide, and titration of the chloride by *N*/10-silver nitrate. The process is applicable to dichloroethylene, but not to chloroform or benzyl chloride. H. W.

Chlorination of Carbon Chains. Chlorination of Normal Butyl Alcohol. H. Gault and R. Guillemet (*Bull. Soc. chim.*, 1923, **33**, [iv], 1792—1801).—The chlorination, at definite temperatures in diffused daylight, of *n*-butyl alcohol has been studied, using iron (steel wire) as a catalyst, and different methods of procedure, viz., either bubbling chlorine through the alcohol, or (counter-current method) allowing the latter to run in a helical path down a vertical tube up which the chlorine passed. A comparative chlorination was carried out, in each case, in absence of the catalyst. The latter does not affect the yield of main product, but diminishes the amounts of by-products. These are produced in larger amount in cold than in hot chlorinations, owing to the formation of acetals in the latter case, and resulting restriction of action.

Chlorination, at temperatures not higher than 10°, by the bubbling method, gave, in presence of iron, a single product (corresponding with 18—20% of the alcohol used), shown to be the *dibutyl acetal* of a *chlorobutaldehyde*, $C_4H_7Cl(OBu)_2$, a colourless liquid, b. p. 125°/15 mm. The latter in presence of hydrogen chloride in a closed tube at 120—130° was partly converted into an unstable *liquid* (b. p. 80—90°/15 mm., with loss of hydrogen chloride) which reduced Fehling's solution and was converted by alcoholic hydrogen chloride into an *acetal*, $CHMeCl\cdot CH_2\cdot CH(OEt)_2$(?).

Chlorination by the bubbling method (using the catalyst) at 40—80° gave the *dibutyl acetal* of a *dichlorobutaldehyde* (yield, 50% of alcohol taken; b. p. 140—142°/15 mm.). This acetal, although unaffected by diluted mineral acids at the ordinary pressure, was partly converted, on heating at 125° in presence of hydrogen chloride, into a *liquid* (b. p. 105—110°/15 mm.) which reduced Fehling's solution, and lost hydrogen chloride on being distilled. The acetal, on being heated with acetic anhydride in a closed tube at 200°, was partly converted into *n*-butyl acetate and a *dichlorobutylidene diacetate* (b. p. 124—129°/15 mm.) (?), and with chromic acid yielded butyric acid and a *butyl dichlorobutyrate* (b. p. 210—215°).

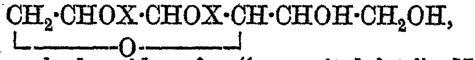
The counter-current method gives less homogeneous products than are given by the bubbling method. E. E. T.

Oleic Alcohol. Y. TOYAMA (*Chem. Umschau*, 1924, **31**, 13—16; cf. A., 1922, i, 895).—The acetyl ester of the oleic alcohol obtained from rabukazame oil gave on oxidation with potassium permanganate nonylic acid and acetylhydroxynonylic acid. This result, coupled with the previously established fact that the same substance gives the acetyl ester of normal octadecyl alcohol on hydrogenation, establishes the formula, $CH_3\cdot[CH_2]_7\cdot CH\colon CH\cdot[CH_2]_7\cdot CH_2\cdot OH$, for oleic alcohol. It is accordingly identical with the alcohol obtained from ethyl oleate. It has d_4^{15} 0·8523, d_4^{20} 0·8491, d_4^{40} 0·8367; n_D^{15} 1·4626, n_D^{20} 1·4607, n_D^{40} 1·4530, b. p. 333—335°/760 mm., 197°/10 mm., 209°/15 mm., 228°/30 mm. Elaidic alcohol has m. p. 35·0—35·5°, d_4^{40} 0·8338, n_D^{40} 1·4522, b. p. about 333°/760 mm., 198°/10 mm., 210°/15 mm., 229—230°/30 mm. These two isomeric alcohols are very stable and show no tendency to change into one another on heating or acetylation. They are sharply differentiated from one another by their melting points. H. C. R.

Equilibria between some Glycols and their Acetone Compounds. J. BÖESEKEN and P. H. HERMANS (*Rec. trav. chim.*, 1923, **42**, 1104—1110).—The authors have prepared the acetone derivatives [*iso*propylidene ethers] of ethylene glycol, propane-αβ-diol, propane-αγ-diol, glycerol, and monochlorohydrin, 1 : 3-*ciscyclo*pentanediol, and 1 : 2-*ciscyclo*hexanediol. The method of preparation used was to heat suitable quantities of the glycol and acetone with sulphuric acid. The following new physical data are recorded: *iso*propylidene ether of ethyleneglycol, b. p. 92·5—92·7°, d_4^{17} 0·9469, n_D^{17} 1·40024, solubility in water, 1 vol. in 3½—4 vols. at 18°; *iso*propylidene ether of propane-αβ-diol, b. p. 98—99°, $n_D^{18\cdot5}$ 1·40191, $d_4^{18\cdot5}$ 0·9090, solubility in water, 1 vol. in 9—10 vols.; *iso*propylidene ether of propane-αγ-diol, b. p. 123—125°, $n_D^{18\cdot5}$ 1·4252, $d_4^{16\cdot5}$ 0·9587; *iso*propylidene ether of α-monochlorohydrin, b. p. 116°/11 mm., $d_4^{17\cdot5}$ 1·322, $n_D^{17\cdot5}$ 1·4820. The molecular weight of these compounds has been determined and is found to show no association of the molecules. The equilibrium constants of the reaction, acetone+

diol ⇌ *iso*propylidene ether + water, have been ascertained in each case, and the values compared with the difference in electrical conductivity of a 0·5 mol. solution of the diol containing 0·5 mol. of boric acid, and the sum of the electrical conductivities of a 0·5 mol. solution of boric acid and a 0·5 mol. solution of the diol. The two sets of figures are parallel, which is taken to indicate that the glycols combine with the same facility with acetone as they do with boric acid. A modification of the Le Bel–Henniger fractionating column was used in the purification of the materials, the bulbs of the original apparatus being connected with capillary tubes instead of the one opening; this causes the outside lateral tubes continuously to contain liquid. J. F. S.

The Condensation of Mannitol with Olive Oil. J. C. Irvine and H. S. Gilchrist (*J. Chem. Soc.*, 1924, **125**, 10—15).—" Mannitol fat " (cf. Lapworth and Pearson, A., 1919, i, 570), prepared by the interaction of mannitol and olive oil in the presence of sodium ethoxide, consists essentially of *mannitan dioleate*, which is formed by the dehydration of *mannitol dioleate*, the first product of the reaction. Further dehydration (at 200° under reduced pressure) results in the formation of iso*mannide dioleate*. Treatment of mannitan dioleate with excess of methyl iodide and silver oxide results only in the formation of *monomethylmannitan dioleate*, together with a trace of *monomethyl*iso*mannide* (n_D 1·4506), from *iso*mannide originally present. On boiling with 0·5% alcoholic hydrogen chloride, monomethylmannitan dioleate gives ethyl oleate and *monomethylmannitan*, a viscous syrup. The latter was methylated to *trimethylmannitan*, a clear, mobile syrup, b. p. 115—120°/0·18 mm., n_D 1·4518. Structural considerations based on the reactions described lead to the formula



$$\underbrace{CH_2\cdot CHOX\cdot CHOX\cdot CH}_{O}\cdot CHOH\cdot CH_2OH,$$

where X is the oleyl residue, for " mannitol fat." No more than two acyl groups can be introduced into the mannitol molecule. F. G. W.

The αγ-Dichloropropyl Ethers and the Corresponding Acetals. W. Dulière (*Bull. Soc. chim.*, 1923, **33**, [iv], 1647—1654; cf. Wohl, A., 1898, i, 555).—The ethers were prepared by saturating an equimolecular mixture of acraldehyde and aliphatic alcohol with dry hydrogen chloride at −10°, the products being purified by distillation under reduced pressure. They are colourless liquids of characteristic odour, decomposing with liberation of hydrogen chloride when heated at atmospheric pressure. They are not miscible with water, but react with it, hydrogen chloride being formed. With aliphatic alcohols, particularly those containing few carbon atoms, they readily produce acetals by reaction with the α-chlorine atom, and with magnesium alkyl halides monochloroethers are obtained. The following are described: *methyl αγ-dichloropropyl ether*, b. p. 45°/12 mm., d^{20} 1·187, n_D^{20} 1·44777, yielding, with methyl alcohol, the acetal *γ-chloro-αα-dimethoxy-*

propane, b. p. 45°/12 mm., d^{20} 1·059, n_D^{20} 1·41631; *ethyl* $\alpha\gamma$*-dichloropropyl ether* has b. p. 56°/12 mm., d^{20} 1·122, n^{20} 1·44235, and γ-chloro-α-diethoxypropane has d^{20} 0·991 (cf. Wohl, *loc. cit.*); *propyl* $\alpha\gamma$*-dichloropropyl ether*, b. p. 65°/12 mm., d^{20} 1·100, n_D^{20} 1·44576, and γ*-chloro-*$\alpha\alpha$*-dipropoxypropane* has b. p. 87°/20 mm., d^{20} 0·972, n_D^{20} 1·42871; $\alpha\gamma$*-dichloropropyl* iso*butyl ether*, b. p. 89°/21 mm., d^{20} 1·067, n_D^{20} 1·44305, and γ*-chloro-*α*-di*iso*butoxypropane*, b. p. 105°/12 mm., d^{20} 0·936; $\alpha\gamma$*-dipropyl* iso*amyl ether*, b. p. 103°/20 mm., d^{20} 1·027, turns brown and decomposes on being kept.

H. J. E.

The Alkyl Titanates. F. Bischoff and H. Adkins (*J. Amer. Chem. Soc.*, 1924, **46**, 256—259).—*Tetramethyl titanate*, prepared from methyl alcohol, sodium, and titanium tetrachloride, crystallising point 209—210°, b. p. 243°(corr.)/52 mm., is rapidly hydrolysed in air. *Tetraethyl titanate*, prepared similarly from ethyl alcohol, had b. p. 205°/156 mm., 145°/8·5 mm., d_{20}^{20} 1·107. *Tetra*iso*propyl titanate*, obtained mixed with 4% of *iso*propyl alcohol as a constant-boiling mixture, has b. p. 230°/740 mm. *Tetra-*n*-butyl titanate* has b. p. 185—187°/16 mm., d_{20}^{20} 0·993. On boiling the higher esters with methyl alcohol, a quantitative yield of the tetramethyl derivative is obtained. All these esters are colourless.

F. A. M.

Octyl Mercaptan. H. Kahn (*Bul. Soc. Chim. România*, 1923, **5**, 70—72).—Pure octane, obtained by the repeated fractionation of benzene from Ploesti and removal of aromatic hydrocarbons by repeated action of a mixture of nitric and sulphuric acids, is converted into octyl chloride, which, when treated with a saturated alcoholic solution of potassium hydrogen sulphide, yields *octyl mercaptan*, a colourless liquid of disagreeable odour, b. p. 198—200°. When heated, it readily decomposes into octyl sulphide and hydrogen sulphide.

J. W. B.

Valeric Acid. S. Koizumi and H. Ichinose (Japan. Pat. 41910).—Valeric acid is prepared from amyl alcohol by electrolytic oxidation in 5—20% sulphuric acid solution at the ordinary temperature. Lead or lead peroxide is used as anode, and platinum, copper, iron, or nickel as cathode, without diaphragm. The addition of 1 g. of oxides of vanadium, chromium, or manganese to 1 litre of the sulphuric acid promotes the reaction. The electrolyte is vigorously agitated during the operation, the current density being 1—5 amp. per sq. dm. The product separates in a nearly pure state, the current yield being above 80%.

K. K.

Palmitic and Stearic Anhydrides. D. Holde, J. Ripper, and F. Zadek (*Ber.*, 1924, **57**, [*B*], 103—104).—Since the constants recorded in the literature for these substances are very discordant, they have been redetermined with material prepared by Albitzky's method as modified by Holde and Tacke (A., 1920, i, 811). Palmitic anhydride has m. p. 64°, d_4^{83} 0·8383, whence d^{15} 0·8832, and n^{100} 1·4679. Stearic anhydride has m. p. 72°, d_4^{80} 0·855, whence d_4 0·897, and n_D^{100} 1·4284.

H. W.

The Composition and Constitution of Elæostearic Acid. L. MAQUENNE (*Bull. Soc. chim.*, 1923, **33**, [iv], 1654—1655).—The author claims priority over Vercruysse (A., 1923, i, 533) and refers to his own work (A., 1903, i, 62) in support of his view that the extreme readiness with which the acid undergoes oxidation has led to errors with regard to its formula and m. p., which are $C_{18}H_{30}O_2$ and 48°, respectively. H. J. E.

Elaidic Acid and its Anhydride. D. HOLDE and K. RIETZ (*Ber.*, 1924, **57**, [*B*], 99—102).—Elaidic acid, obtained by the action of nitrous acid on oleic acid, crystallises in colourless, lustrous leaflets, m. p. 44·4° (corr.), n_D^{100} 1·4308. Elaidic anhydride, prepared from the acid and acetic anhydride, has m. p. 46·4° (corr.), d_{15}^{82} 0·8476, d_{15}^{93} 0·8396, d_4^{100} 0·8338, n_D^{100} 1·4339.

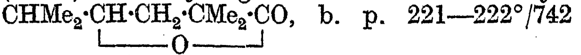
The electrolytic conductivities of oleic and elaidic acids and their anhydrides in very highly purified acetone have been measured. Little differences are observed between the constants of the acids and their anhydrides, but those of elaidic acid and its anhydrides are somewhat higher than those of the oleic compounds. H. W.

The Relative Solubilities of the Calcium and Magnesium Salts of the Higher Fatty Acids. W. BILTZ and W. RÖHRS (*Z. angew. Chem.*, 1923, **36**, 609—611).—A study of the equilibria resulting from the action of solutions of calcium chloride on solid magnesium stearate and oleate. The mixture was heated for one hour, cooled, and filtered, the extent of double decomposition being found from analysis of the filtrate. When equimolecular proportions were used, the amounts of calcium stearate and oleate produced were 88% and 81%, respectively; these values increased to 98% and 90% on doubling the molecular ratio of calcium chloride. Fractional precipitation of a mixture of equivalent quantities of calcium and magnesium chlorides with potassium stearate and oleate yielded mainly calcium salt (Ca 6·54%, Mg 0·03%). Experiments on commercial soap are also described. The general conclusion is drawn that calcium stearate is considerably and calcium oleate appreciably less soluble than the corresponding magnesium salts. H. J. E.

The Composition of Whale Oil. C. H. MILLIGAN, C. A. KNUTH, and A. S. RICHARDSON (*J. Amer. Chem. Soc.*, 1924, **46**, 157—166).—Whale oil is shown to contain a complicated mixture of fatty acids having 14 to 22 carbon atoms, probably with a small amount of C_{24} acids. The highly unsaturated acids are chiefly those containing 20 and 22 carbon atoms. The percentage composition of the mixture of fatty acids is approximately: (C_{14}) myristic 4·5; (C_{16}) palmitic 11·5, palmitoleic 17·0; (C_{18}) stearic 2·5, unsaturated (nearly all oleic) 36·5; (C_{20}) unsaturated 16; (C_{22}) unsaturated 10; (C_{24}) unsaturated 1·5; unsaponifiable 0·7. F. A. M.

The Catalytic Hydrogenation of some Unsaturated Compounds, especially Oils, by Means of Nickel at the Ordinary Temperature. M. TANAKA (*Chem.-Ztg.*, 1924, **48**, 25—26).—The author has extended the work of Kelber (A., 1916, ii, 309, 609) by using nickel, precipitated on kieselguhr, for reduction at the ordinary temperature of ethyl cinnamate, cinnamaldehyde, cinnamyl alcohol, azoxybenzene (to azobenzene, hydrazobenzene, and aniline), ricinostearol di-iodide, perilla oil, hemp-seed oil, chrysalis oil, and shark oil. Details of the amounts of hydrogen fixed are given and also of similar experiments carried out with a palladium catalyst for comparison. [Cf. *B.*, Mar.] H. J. E.

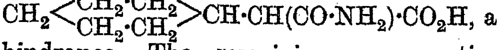
Reaction of Zinc on Mixtures of Ethyl α-Bromo*iso*butyrate and Aldehydes or Ketones. I. Coucoulesco (*Bul. Soc. Chim. România*, 1923, **5**, 63—70).—The action of zinc on mixtures of ethyl α-bromo*iso*butyrate with *iso*valeraldehyde, *iso*propyl ketone, and acetophenone, respectively, has been studied. With *iso*valeraldehyde, the reaction takes the normal course and yields *ethyl* β-*hydroxy-*αα*δ-trimethylhexoate* (b. p. 173—175°/140—145 mm.), which is hydrolysed to β-*hydroxy-*αα*δ-trimethylhexoic acid*, colourless tetragonal or hexagonal crystals, m. p. 81°, α=0·00147. The acid is soluble in alcohol and in ether. The *barium*, *silver*, *potassium*, *zinc*, and *lead* salts are described. The action either of dilute sulphuric acid (1 : 10) or of hydrogen iodide on this acid yields the γ-*lactone*,



$CHMe_2{\cdot}\underbrace{CH{\cdot}CH_2{\cdot}CMe_2{\cdot}CO}_{O}$, b. p. 221—222°/742 mm., probably owing to the initial formation of the βγ-unsaturated acid. Oxidation of the acid with potassium permanganate yields only unchanged material, carbon dioxide, and water.

With the two ketones, the main products isolated are ethyl *iso*butyrate, unchanged ketones, and a small quantity of oil, which is probably the expected ester of the hydroxy-acid. This on hydrolysis yielded an acid oil from which a pure substance could not be isolated. J. W. B.

Synthesis of the Higher Monoalkylmalonic Acids. (Mrs.) G. M. Robinson (*J. Chem. Soc.*, 1924, **125**, 226—231).—A method for the preparation of higher monoalkylmalonic acids, suitable for use with considerable quantities of material in one operation, and in which the formation of the corresponding dialkyl acids is minimal, is as follows. A mixture of the higher alkyl iodide (1 mol.), ethyl cyanoacetate (2 mols. or more), and potassium carbonate (1·5 mols.) is boiled under a reflux condenser and at a reduced pressure until the reaction is completed. The unchanged cyanoacetate is then recovered by distillation, the whole residue hydrolysed with hot 20% sodium hydroxide, and the product precipitated with dilute sulphuric acid. Under these conditions, the hydrolysis of α-cyano*cyclo*hexylacetic acid yielded only the malonamic acid,



$CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}CH{\cdot}CH(CO{\cdot}NH_2){\cdot}CO_2H$, a result ascribed to steric hindrance. The remaining cyanoacetic acids examined were completely hydrolysed to the corresponding malonic acids. *cyclo-Hexylmalonamic acid*, colourless needles, m. p. 184°, was unattacked on heating for four hours with alcoholic potassium hydroxide.

Heated in a tube, it loses carbon dioxide and forms *cyclo*hexylacetamide.

The preparation of *n*-heptylmalonic acid, *n*-octylmalonic acid, rhombic prisms, m. p. 115°, n-*undecylmalonic acid*, rectangular needles, m. p. 108°, and *n*-hexadecylmalonic acid, m. p. 119°, is described in detail.

n-*Decyldimethylcarbinol*, obtained from methyl undecoate and magnesium methyl iodide, is a mobile liquid, b. p. 145°/10 mm.

F. G. W.

The Chlorosulphides of Carbon. Decomposition in Presence of Iron. M. DELÉPINE and J. GIRON (*Bull. Soc. chim.*, 1923, **33**, [iv], 1785—1792).—The chlorosulphides of carbon, when left in contact with metallic iron, are converted into sulphur and carbon tetrachloride. The action is catalytic, the iron suffering very little alteration. The chlorosulphides examined were: thiocarbonyl chloride, perchloromethyl mercaptan (also examined in presence of carbon disulphide and/or sulphur chloride), and the chlorosulphides represented by the formulæ: (1) $CCl_3{\cdot}S{\cdot}CS{\cdot}Cl$, (2) $CCl_3{\cdot}S_3{\cdot}CCl_3$, and (3) $C_2Cl_6S_4$ (obtained from the residue in the distillation of perchloromethyl mercaptan, and having b. p. 150—154°/26 mm.).

E. E. T.

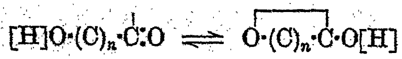
Condensation of Citral with Ketones and Synthesis of some New Ionones. H. HIBBERT and L. T. CANNON (*J. Amer. Chem. Soc.*, 1924, **46**, 119—129).—Citral, purified by a modification of Tiemann's method (A., 1899, i, 622), was condensed with acetone by means of sodium ethoxide, giving a 55% yield of pure ψ-ionone. The best condensing agent for converting ψ-ionone into α-ionone was found to be 85% phosphoric acid. *ψ-Ethylionone*, prepared from citral and methyl propyl ketone, is a pale yellow oil, b. p. 155—158°/8 mm.; its structure is probably $Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}Pr$. It is converted by means of 85% phosphoric acid into *ethylionone*, a pale yellow oil, b. p. 138—140°/8 mm., possessing a pleasant odour of violets.

Citral condenses with acetophenone, in presence of sodium ethoxide, to form *phenyl-ψ-ionone*, an odourless, viscous, pale yellow oil, b. p. 182—185°/4 mm. *Phenylionone*, prepared from it by the action of 85% phosphoric acid, is a pale yellow, viscous oil, b. p. 172—175°/4·5 mm., with a very faint but rather disagreeable odour, the violet fragrance being almost entirely suppressed.

Attempts to condense citral with diethyl ketone or dipropyl ketone were unsuccessful.

F. A. M.

Ring-chain Tautomerism. IX. The Mutarotation of the Sugars. J. W. BAKER, C. K. INGOLD, and J. F. THORPE (*J. Chem. Soc.*, 1924, **125**, 268—291).—A proof, from a dynamical investigation and survey of structural evidence, supported by data from two series of crucial experiments, that the mutarotation of the sugars is a case of ring-chain tautomerism in the sense



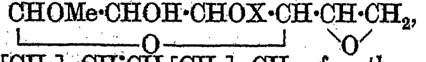
$$[H]O{\cdot}(C)_n{\cdot}\overset{|}{C}{:}O \rightleftharpoons O{\cdot}(C)_n{\cdot}C{\cdot}O[H]$$

on lines suggested by Jacobson and Stelzner (Meyer and Jacobson's "Organischen Chemie," 2 Aufl., 1, **2**, 886, 910, 915, 927), and not dependent on the intermediate formation of hydrates as suggested by Lowry (T., 1903, **83**, 1316) and Armstrong (T., 1903, **83**, 1309). It is postulated that the phenomenon is of the same nature in all cases and not of varying kinds as suggested by Irvine and Steele (T., 1915, **107**, 1239—1240). The full mathematical derivation of the form and spacing of the mutarotation–time curves on the mutarotation–time–concentration diagram, according to the tautomeric-hydrogen theory, is given. It is deduced that whilst the form of the mutarotation–time curves can be accommodated by the intermediate-hydrate theory, the spacing of curves obtained from measurements of mutarotation in presence of varying initial concentrations of water is zero, in direct contradiction of the consequences of the hydrate theory, and in agreement with the experimental results. From structural considerations, it is pointed out that whilst *d*-fructose should not be capable of mutarotation according to Armstrong's theory, its mutarotation has actually been measured in water, pyridine, and formamide solutions, and that *d*-glucoseoxime, *d*-glucoseanilide, *d*-glucoseimine, *d*-glucosephenylhydrazone, and ethylamino-*d*-glucose, all show mutarotation contrary to expectations based on Lowry's views. Also, no substance which, according to all three theories, should be incapable of mutarotation, has been found to exhibit this phenomenon, although interconversion of isomeric forms can sometimes be effected by reagents. This is shown to be at variance with Armstrong's views, and it is suggested that the mechanism of such conversions is fundamentally different from that of mutarotation. Experimentally, the mutarotation of tetra-acetyl-*d*-glucose in ethyl acetate solution at 44·8° was measured under conditions such that water was rigorously excluded, or present in small, accurately known concentrations of 0·025, 0·05, and 0·1%, respectively, these amounts being small in proportion to that possibly present in the dried materials. The velocity constants were, respectively, 0·0222, 0·0221, 0·0209, and 0·0208, *i.e.*, independent of the small initial concentration of water. The mutarotation of α-*d*-glucose in methyl alcohol was also measured at the same temperature, first with dried materials, and then in presence of 0·5, 1·0, and 2·0%, respectively, of added water, these concentrations of water being relatively large in comparison with that which might have been present originally. The initial velocities were, respectively, 0·165, 0·178, 0·246, and 0·379. These values are not in proportion to the initial concentration of the water, as the hydrate theory demands. F. G. W.

Oxidation of Dextrose by Iodine in the Presence of Insulin. G. A. Alles and H. M. Winegarden (*J. Biol. Chem.*, 1923, **58**, 225—234).—The rate of oxidation of dextrose by iodine is not altered by the presence either of insulin alone or of insulin plus liver extract, blood-serum, or oxalated blood. Since the rates of oxidation of the various sugars differ greatly, it is evident that, under the conditions employed, insulin does not transform dextrose into a more reactive form (cf. Winter and Smith, A., 1923, i, 513). E. S.

A Quantitative Study of the Interaction of Dextrose and Phenylhydrazine. E. Knecht and F. P. Thompson (*J. Chem. Soc.*, 1924, **125**, 222—226).—In view of the strong reducing properties of phenylhydrazine and its resistance to reduction by titanous chloride, the reaction between phenylhydrazine and dextrose was studied to confirm quantitatively the formation of aniline and ammonia simultaneously with the osazone, and to discover the fate of the reactants in view of the low yields of osazone usually obtained. Pure dextrose (1 mol. : 3·6 g.) and phenylhydrazine (3 mols. : 6·48 g.) were dissolved in a mixture of water (190 c.c.) and glacial acetic acid (10 c.c.) and heated for three hours on the water-bath. A parallel experiment was made using *p*-nitrophenylhydrazine, but at twice the dilution of dextrose and phenylhydrazine. The osazone was filtered off and weighed. The unchanged phenylhydrazine was determined by boiling with Fehling's solution and measuring the nitrogen evolved, and the ammonia by a distillation during which tarring was avoided. The amount of ammonia produced in both cases was in agreement with that calculated from the weight of osazone obtained, in accordance with Fischer's equation, but it is inferred that a portion of the dextrose remains in solution as phenylhydrazone. The addition of aniline acetate or ammonium acetate to the reaction mixture increases the yield of osazone. By heating 3·6 g. of dextrose and 6·48 g. of phenylhydrazine with 20 c.c. of glacial acetic acid diluted to 100 c.c. with water, for three hours at water-bath temperature, a yield of osazone corresponding with 84% of the theoretical may be obtained. F. G. W.

A Synthetic Fat containing a Methylglucoside Residue. J. C. Irvine and H. S. Gilchrist (*J. Chem. Soc.*, 1924, **125**, 1—10).—When olive oil (1 mol.) is heated with α-methylglucoside (3 mols.) in presence of sodium ethoxide at 140°, *methylglucoside mono-oleate* is formed, and this on further heating at 220°/12 mm. loses water and forms *anhydro-methylglucoside mono-oleate*, a viscous, yellow oil, $[\alpha]_D^{15} + 38°$ in chloroform. Attempts to introduce more than one oleyl residue failed. Treatment of the anhydro-mono-oleate with methyl iodide and silver oxide gave *monomethyl-anhydro-methylglucoside mono-oleate*, a mobile, yellow oil; this on boiling with methyl-alcoholic hydrogen chloride gave methyl oleate and *monomethyl-anhydro-methylglucoside*, a colourless, viscous syrup. The latter was further methylated to *dimethyl-anhydro-methylglucoside*, b. p. 115—120°/0·2 mm., n_D 1·4419, and hydrolysed with barium hydroxide to *monomethyl methylglucoside*, a colourless, viscous syrup. Further hydrolysis with 5% hydrochloric acid at 100° gave a syrupy monomethylglucose. Consideration of the reactions described leads to the formula,



$$\underbrace{CHOMe\cdot CHOH\cdot CHOX\cdot CH}_{O}\cdot \underbrace{CH\cdot CH_2}_{O},$$

where $X{=}CO\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_7\cdot CH_3$, for the methylglucoside fat. F. G. W.

Fluoroacetyl Derivatives of Sugars. II. Optical Rotation and Atomic Dimension. D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1923, **45**, 2381—2390).—In comparing the optical rotations of monohalogen-acetyl derivatives of dextrose, cellose, xylose, and lævulose, the differences F–Cl, Cl–Br, Br–I are found to be approximately proportional to the differences in atomic diameter. This simple relation holds for the specific, but not for the molecular rotation. *Fluorotetra-acetyl-lævulose* is obtained from β-penta-acetyl-lævulose. It is readily soluble in chloroform, and has m. p. 112°, $[\alpha]_D^{20}$ −90·43° in chloroform. It is stable, colourless, and odourless. *Bromotetra-acetyl-lævulose* was prepared by the action of a solution of hydrogen bromide in glacial acetic acid on a solution of β-penta-acetyl-lævulose in the same solvent. It is a very unstable, crystalline solid, $[\alpha]_D^{20}$ −189·1° in chloroform, m. p. 65°. When preserved, it is transformed into β-tetra-acetyl-lævulose. F. G. P.

Unsaturated Reduction Products of the Sugars and their Transformations. VIII. M. BERGMANN [and, in part, H. SCHOTTE, E. RENNERT, S. LUDEWIG, and M. KOBEL] (*Annalen*, 1923, **434**, 79—110).—Fischer and Curme (A., 1914, i, 931) obtained a substance, which they described as lactal, by the hydrolysis of hexa-acetyl-lactal by means of barium hydroxide. This product had 1 mol. of water of crystallisation, $[\alpha]_D$ +26·77° to +26·95°, m. p. 184—186°, or, when anhydrous, m. p. 165—170°. Lactal prepared by using methyl-alcoholic ammonia instead of barium hydroxide is anhydrous, and has $[\alpha]_D^{16}$ +27·66° to +27·67°, m. p. 192° (corr.), decomp. about 212°. A sample so prepared is not changed on standing with barium hydroxide solution at 37° for two or three days. Lactal prepared by means of ammonia is reconverted by the action of acetic anhydride and pyridine into the hexa-acetate, m. p. 114°, but the product from "baryta-lactal" has m. p. 108—109°. It is thought that Fischer and Curme's material was simply impure lactal.

When lactal is boiled with water, the product has m. p. 198° (corr.), $[\alpha]_D^{17}$ +36·43°, but the other properties are, in general, unchanged.

Hexa-acetyl-lactal is converted by boiling with water into *ψ-lactal penta-acetate*, a heavy, snow-white powder (flat tablets, small, thin prisms, or elongated, hexagonal crystals), m. p. 123—124° (corr.) after previously softening, decomp. 190°. The structure of this compound is different from that of lactal or its hexa-acetate, because on treatment with acetic anhydride and pyridine it gives *ψ-lactal hexa-acetate*, aggregated prisms or needles, m. p. 127—128° (corr.), $[\alpha]_D^{18}$ +32·24°, which is reconverted, by boiling with water, into the penta-acetate. Both the penta- and the hexa-acetate of ψ-lactal have a bitter taste; the hexa-acetate does not give the pine-shaving reaction, and does not react with bromine, but it reduces ammoniacal silver nitrate solution, and gradually gives a red coloration with magenta–sulphurous acid. In its sensitiveness to even dilute mineral acids it resembles lactal and the deoxy-sugars.

When ψ-lactal penta-acetate is treated successively with cold methyl-alcoholic hydrogen chloride, sodium hydroxide solution (with cooling), and sodium hydroxide and methyl sulphate, a yellow syrup is obtained, b. p. 178—180°/0·3—0·4 mm., $n_D^{50·5}$ 1·4661; this is the *pentamethyl* ether of a *compound*, $C_{12}H_{20}O_9$, isomeric with lactal. This series of reactions may involve a change of structure. When ψ-lactal penta-acetate is treated at 0° with a saturated solution of hydrogen bromide in glacial acetic acid, two molecular proportions of hydrogen bromide are taken up, giving a *dibromide*, $C_{22}H_{30}O_{13}Br_2$, small prisms or needles, m. p. 124° (corr.) (decomp.), $[\alpha]_D^{23}$ +69·6°. The latter is converted by means of silver carbonate in moist acetone solution into a *hydroxybromide*, $C_{22}H_{30}O_{13}Br(OH),\frac{1}{2}H_2O$, snow-white, glistening flakes, m. p. 87—88° after sintering at 80°, decomp. 110°. In dry methyl-alcoholic solution, the product is the corresponding *methoxybromide*, m. p. 147—148° (corr.), with subsequent decomposition, which is hydrolysed by means of methyl-alcoholic ammonia to the free *bromomethoxy*-derivative, snow-white, aggregated needles, m. p. 119° (decomp.). ψ-Lactal penta-acetate, which need not be isolated, is converted by the action of cold barium hydroxide solution into iso*lactal*, short, slender needles, which is very difficult to purify. It has a vigorous reducing action on Fehling's solution, and gives a green coloration with a pine shaving. With warm alkali, it becomes yellow or brown, whilst concentrated mineral acids give a red solution; it is not attacked by perbenzoic acid. *iso*Lactal has a slightly sweet taste, resembling that of lactose. The action of acetic anhydride and pyridine on *iso*lactal gives iso*lactal hexa-acetate*, rhombic prisms, or leaflets, m. p. 166—167° after sintering at 163°, $[\alpha]_D^{23}$ +55·30°, which gives the pine-shaving test, and has an insipid taste. By the action of boiling water, one acetyl group is eliminated. *iso*Lactal may be acetalised by means of methyl-alcoholic hydrogen chloride, or methylated by means of methyl sulphate; it is rapidly oxidised by means of aqueous bromine.

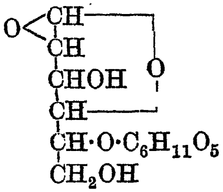
The action of perbenzoic acid, in warm ethyl acetate solution, on an aqueous solution of lactal gives 5-*galactosidomannose*, needles, m. p. 196—197° (corr.), after slight softening. This compound has, initially, $[\alpha]_D^{23}$ +23° (about), rising to +30° after eighty minutes. It reduces Fehling's solution immediately, and reacts gradually with ammoniacal silver nitrate solution or magenta and sulphurous acid. With phenylhydrazine, it gives lactosazone; it is decomposed by emulsin.

The diacetate, obtained by boiling triacetylglucal with water, is converted by heating with acetic anhydride and sodium acetate at 100° into *ψ-glucal triacetate*, a colourless liquid, b. p. 150—165°/0·2—0·3 mm., which has a bitter taste and a pungent odour. It is reconverted by the action of boiling water into the diacetate, which is described as ψ-glucal diacetate. The triacetate is highly sensitive to the action of acids, and immediately becomes brownish-black when treated with cold alkali. It gives an intensely green coloration with a pine shaving, and reacts with magenta–sulphurous acid, Fehling's solution, or ammoniacal silver nitrate. With bromine in chloroform solution at 18°, two atoms of halogen are absorbed, one of which may then be removed by boiling with silver carbonate and dry methyl alcohol. The action of 1% methyl-alcoholic hydrogen chloride on ψ-glucal diacetate gives a pale yellow syrup, from which the following fractions are isolated. (1) A colourless, mobile liquid, b. p. 68—69°/0·3 mm., n_D^{20} 1·4763, $[\alpha]_D^{22}$ +1·2°, apparently $C_7H_{10}O_3$, and perhaps the methyl*cyclo*-acetal of a hydroxyaldehyde, with two bonds, and a methylene group adjacent to the acetalised aldehyde group. (2) A viscous, slightly yellow oil, b. p. 88—90°/0·1 mm., n_D^{20} 1·4984, $[\alpha]_D^{20}$ +15·50—+16·1°, evidently $C_8H_{12}O_4$. (3) A viscous, colourless liquid, apparently $C_7H_{12}O_4$, b. p. 120—121°/0·2 mm., n_D^{20} 1·4860, $[\alpha]_D^{20}$ +71·7—+72·2°. Each of these fractions gives a green pine-shaving reaction, and is sensitive to acids; Fehling's solution is not reduced. The action of cold barium hydroxide solution on ψ-glucal diacetate gives iso*glucal*, a syrup, b. p. 120—130°/0·2—0·3 mm. (but sublimes at about 60° at this pressure), $[\alpha]_D^{23}$ +43·15°, which is isolated as its *phenylbenzylhydrazone*, microscopic needles, m. p. 121—122°, $[\alpha]_D^{22}$ −22·38°, from which it is regenerated by boiling with aqueous benzaldehyde or concentrated formaldehyde solution, the former being preferable. *iso*Glucal is readily decomposed by means of acids or of alkali. It gives a very pronounced green coloration with a pine shaving, and vigorously reduces Fehling's solution. On keeping the syrupy material in a vacuum, *crystals* are gradually deposited, m. p. 49—50°, $[\alpha]_D^{18}$ +45·6°, which, in contrast with the original material, do not give a coloration with magenta–sulphurous acid. The syrupy *iso*glucal rapidly reacts with bromine, but in chloroform solution the reaction is apparently incomplete. Neutral or alkaline permanganate solution is immediately decolorised, but perbenzoic acid is not attacked.

Acetobromomaltose is reduced by means of zinc dust and 50% acetic acid, giving a poor yield (50%) of impure acetomaltal. The latter, when boiled with water, gives *penta-acetylmaltal hydrate*, needles, m. p. 173—174° (corr.); when acetylated, it gives a *hexa-acetate*, m. p. 155—157°. The elimination of the acetyl groups from acetomaltal, followed by oxidation using perbenzoic acid, gives a disaccharide containing mannose, perhaps 6-glucosidomannose (details will be given later).

When a solution of rhamnal in *N*-sulphuric acid is continuously extracted with ether at 35°, a yellow liquid is removed; the aqueous solution then contains l-*rhamnodeose* (2-*deoxy*-l-*rhamnose*), a colourless liquid. This substance is very readily decomposed by the action of mineral acids. It gives the pine-shaving reaction, and reduces Fehling's solution. It is converted by keeping at 20° with methyl-alcoholic hydrogen chloride into its *methyl*cyclo*acetal*, b. p. 120—130°/0·2 mm., which undergoes fission when boiled with aqueous hydrochloric acid. When rhamnodeose is oxidised by means of aqueous bromine solution, the product is *rhamnodesonic* *acid*, which is isolated as its *barium* salt, colourless needles, or as the *phenylhydrazide*, m. p. 172—172·5° (corr.). Kiliani's digitoxose is therefore not identical with *l*-rhamnodeose.

It is proposed (cf. Bergmann, Schotte, and Lechinsky, A., 1922, i, 227) that, in naming a reducing disaccharide, the name of the sugar containing the intact aldehydic group should end in "ose," whilst the second constituent should be named as a glucosidic substituent, *e.g.*, 5-galactosidomannose. If both the reducing groups are glucosidically bound, as in trehalose, a name such as glucosidoglucoside is advocated. Thus sucrose becomes glucosidofructoside, or, alternatively, fructosidoglucoside, but raffinose is called galactosido-(glucosidofructoside). The terms anhydro-sugar, anhydrobiose, etc., are only employed when the aldehyde group, or its half-acetal form, is not involved in the anhydrisation; otherwise, one speaks of monose-anhydride, disaccharide-anhydride, etc. The points of attachment of the oxygen bridge are indicated by means of bracketed numbers. Thus the substance having the annexed formula is designated 5-galactosidomannose-anhydride [1 : 4] [1 : 2]. W. S. N.



The Action of Iodine on Several Carbohydrates. J. Vintilescu and D. Faltis (*Bul. Soc. Chim. România*, 1923, **5**, 59—63).—When powdered iodine is heated (in a steam bath) in a sealed tube with solutions of sucrose, invert-sugar, dextrose, lævulose, lactose, dextrin, glycogen, or gum arabic, the iodine passes slowly into solution during the first period of heating, and is completely converted into hydriodic acid, the solution becoming colourless. On prolonged heating, decomposition of the carbohydrate occurs, with the formation of formaldehyde, formic acid, and a brown oxidation product of the sugar. The iodine is transformed more easily by sugars containing lævulose and progressively slowly by dextrose, lactose, dextrin, glycogen, and gum arabic; the period of heating necessary to cause the same amount of final decomposition follows the same order. The reaction is more rapid the greater the concentration of the sugar solution. The action of hydriodic acid on the carbohydrates is found to be similar, but the destruction of reducing sugars formed is slower than is the case when iodine is added directly. [Cf. *B.*, 1924, 190.] J. W. B.

Wood Cellulose. E. Heuser and S. S. Aiyar (*Z. angew. Chem.*, 1924, **37**, 27—28).—The hypothesis of the identity of cellulose obtained from different sources is supported by experiments with cotton cellulose and wood cellulose. Both specimens give the same yield of pure cellulose triacetate on acetylation with glacial acetic acid, acetic anhydride, and sulphuryl chloride (cf. Barnett, A., 1921, i, 164), and on further treatment with methyl alcohol and hydrogen chloride (cf. Irvine and others, T., 1920, **117**, 1489; 1922, **121**, 1585) both triacetates give the same yield of the same α-methylglucoside. Hydrolysis of both samples of cellulose with 72%

sulphuric acid (cf. Ost and Wilkening, A., 1910, i, 364) and recovery of the dextrose (cf. Monier-Williams, T., 1921, **119**, 803) gives the same yield of crystalline dextrose. W. T. K. B.

The Constitution of Polysaccharides. VII. Esparto Cellulose. J. C. IRVINE and E. L. HIRST (*J. Chem. Soc.*, 1924, **125**, 15—25).—The amount of furfuraldehyde produced by the action of hydrochloric acid on esparto cellulose corresponds with the presence of 18·5% of pentosan in the dry, bleached material. This pentosan can be completely extracted with boiling 12% sodium hydroxide, and was identified as xylan by hydrolysis, in 2% sulphuric acid at 90°, to xylose. The total yield of xylose, based on optical measurements, was 75%, and the nett yield of crystalline material 35—50%, m. p. 143—144°. The latter yielded on methylation the same trimethyl β-methylxyloside as has previously been obtained from xylose. The formation of furfuraldehyde during the hydrolysis of the xylan could not be prevented. The remaining 81·5% of the esparto cellulose, after complete extraction of the pentosan with alkali, gave on acetylation cellobiose octaacetate, and on methylation a trimethyl derivative from which 2 : 3 : 6-trimethylglucose was obtained on hydrolysis, thereby establishing the identity of the alkali-extracted material with cotton cellulose. The original esparto cellulose is more resistant to acetylation than cotton cellulose; the acetate was prepared by incorporating the material with glacial acetic acid containing a little chlorine, adding acetic anhydride, and then passing in a little sulphur dioxide and stirring, when a clear solution was obtained after twenty-four hours. The yield of acetate corresponds with 97·2% of the theoretical, assuming that the pentosan forms a diacetate and the remainder a triacetate. The acetate is softer and more sensitive to high temperature than that of cotton cellulose. On treatment with 1·5% methyl-alcoholic hydrogen chloride at 130° for 120 hours, the acetate yields a mixture of α- and β-methylglucoside and α- and β-methylxyloside, from which pure α-methylglucoside was isolated by crystallisation from alcohol. It is concluded that esparto cellulose is a mixture of 81·5% of hexose cellulose and 18·5% of pentosan, probably in the form of a solid solution. F. G. W.

Starch Iodide. A. LOTTERMOSER (*Oesterr. Chem. Ztg.*, 1924, **27**, 13; cf. A., 1922, i, 10).—Experiments are mentioned on the adsorption of tri-iodion, iodion, and iodine by starch. The curves obtained are typical adsorption isotherms. In the reaction between starch and iodine in the presence of potassium iodide, there is probably an initial adsorption followed by a further slow combination. G. W. R.

Lignosulphonic Acid and the Lactone of Waste Sulphite Liquors. S. V. HINTIKKA (*Cellulosechemie*, 1923, **4**, 93—94).—Salts of α-lignosulphonic acid with primary amines were prepared by separating the sodium lignosulphonate by salting out from waste sulphite liquors and precipitating the aqueous solution of the product with α-naphthylamine sulphate, β-naphthylamine hydrochloride, and *o*-toluidine salt. Klason (A., 1922, i, 324) has considered the α-naphthylamine compound to be a normal ammonium salt of the sulphonic acid, and the β-naphthylamine compound a cyclic internal salt coupling the sulphonic acid and the aldehyde groups. The behaviour of these compounds towards 5% sodium hydroxide at 50° has been studied, the liberated amine being removed by extraction with ether and the lignosulphonic acid reprecipitated by acidification. No difference in the behaviour of these amine salts could be detected; the regenerated lignosulphonic acids were similar in appearance and contained only small residues of nitrogen. The crystalline substance isolated by Holmberg (A., 1921, i, 849) from waste sulphite liquors and described as a lactone has been further investigated. It occurs in the liquors from the digestion of spruce wood, but could not be detected in those from pine wood or from spruce bark. In the digestion of spruce wood, this lactone can be isolated in substantial quantity from the liquor in the early stages of digestion, but the quantity decreases towards the end of the process. J. F. B.

Preparation of Methylamine. M. SOMMELET (*Compt. rend.*, 1924, **178**, 217—219).—Methylamine hydrochloride, prepared by the methods of Brochet and Cambier or of Werner (cf. T., 1917, **111**, 844), is found to contain ammonium chloride and trimethyltrimethylenetriamine hydrochloride. It may be obtained pure by rendering alkaline, extracting with benzaldehyde, distilling the resulting benzylidenemethylamine (b. p. 180°), hydrolysing the latter with hydrochloric acid, washing the methylamine hydrochloride so obtained with alcohol to remove traces of the triamine salt, and finally crystallising twice from 88% alcohol. Pure methylamine hydrochloride has m. p. (in closed tube) 232—233·5° (corr.). E. E. T.

Tetrachloro-iodides of Organic Bases. F. D. CHATTAWAY and F. L. GARTON (*J. Chem. Soc.*, 1924, **125**, 183—188).—Stable tetrachloro-iodides of most organic bases can be prepared by dissolving the base in strong hydrochloric acid, adding an equivalent quantity of iodine, and passing excess of chlorine into the solution. The iodine gradually dissolves with evolution of heat and the tetrachloro-iodide separates either immediately or on allowing the solution to cool in a current of chlorine. The yields are generally quantitative. The tetrachloro-iodides are all golden-yellow, crystalline compounds, soluble in water with slight decomposition. They may be recrystallised from suitable solvents, to which the addition of a little iodine trichloride is sometimes necessary to prevent dissociation. They have sharp melting points, at which decomposition generally takes place, but appear to soften about 20° below the melting point. Heated at higher temperatures, they evolve chlorine, iodine monochloride, and iodine, and leave a residue of the chloride of the base. They can be stored unchanged for at least a month in dry air or in a vacuum over lime. The iodine atom appears to act as the central atom of the negative ion, the four chlorine atoms being arranged tetrahedrally around it, the general formula thus becoming similar to that usually assigned to the chloroaurates. *Guanidine tetrachloro-iodide*, $NH:C(NH_2)\cdot NH_3ICl_4$, golden-yellow, flattened prisms, m. p. 163°. *Carbamide tetrachloro-iodide*, $NH_2\cdot CO\cdot NH_3\cdot ICl_4,H_2O$, long, pale yellow needles, m. p. 73°. The tetrachloro-iodides of pyridine, quinoline, etc., are so sparingly soluble that for their preparation it is necessary to dissolve the iodine in hydrochloric acid by means of a current of chlorine before adding the base. *Pyridinium tetrachloro-iodide*, pale yellow, flattened prisms, m. p. 205° (decomp.). *α-Picolinium tetrachloro-iodide*, bright yellow, flattened prisms showing multiple twinning, m. p. 166° (decomp.). *Collidinium tetrachloro-iodide*, $C_5H_2Me_3N,HICl_4$, orange-yellow, long, flat, rhombic prisms, m. p. 94°. *Quinolinium tetrachloro-iodide*, $C_9H_7N,HICl_4$, pale yellow prisms, m. p. 195° (decomp.). 8-*Methylquinolinium tetrachloro-iodide*, $C_9H_6MeN,HICl_4$, long, pale yellow, hair-like crystals, m. p. 152° (decomp.). 6-*Nitroquinolinium tetrachloro-iodide*, $NO_2\cdot C_9H_6N,HICl_4$, dull yellow, elongated plates, m. p. 131° (decomp.). 2-*Chloroquinolinium tetrachloro-iodide*, $C_9H_6ClN,HICl_4$, pale yellow, flattened prisms, m. p. 143° (decomp.). 6-*Chloroquinolinium tetrachloro-iodide*, dull yellow, crystalline powder, m. p. 131° (decomp.). *Quinaldinium tetrachloro-iodide*, $C_9H_6MeN,HICl_4$, dull yellow, dendriform crystals, m. p. 149° (decomp.). *Caffeine tetrachloro-iodide*, $C_8H_{12}O_2N_4,HICl_4$, pale yellow, crystalline powder, m. p. 134° (decomp.). *Piperidinium tetrachloro-iodide*, $C_5H_{10}NH,HICl_4$, exists in two polymorphic forms; it crystallises from acetic acid in canary-yellow, fern-like crystals, which change on standing in contact with the mother-liquor into compact, six-sided, orange-yellow prisms. Both forms melt at 102° (decomp.). *Piperazine* bis-*tetrachloro-iodide*, $HICl_4,C_4H_{10}N_2,HICl_4$, bright yellow, compact prisms with domed ends, darkens on heating above 100°, and loses iodine trichloride at 160°; iodine is liberated at 195°, a black charred residue remaining. *Pyridine-betaine tetrachloro-iodide*, $C_5H_5N(ICl_4)\cdot CH_2\cdot CO_2H$, bright yellow, compact, six-sided prisms, m. p. 133° (decomp.). Semicarbazide does not form a tetrachloro-iodide, but is decomposed by a solution of $HICl_4$ into nitrogen, carbon dioxide, and ammonium tetrachloro-iodide. *Methylammonium tetrachloro-iodide*, $CH_3\cdot NH_2,HICl_4$, long, golden-yellow, hexagonal prisms with domed ends, m. p. 96° (decomp.). *Dimethylammonium tetrachloro-iodide*, $(CH_3)_2NH,HICl_4$, compact, orange-yellow prisms, m. p. 82° (decomp.). *Trimethylammonium tetrachloro-iodide*, canary-yellow plates, m. p. 182° (decomp.). *Ethylammonium tetrachloro-iodide*, $C_2H_5\cdot NH_2,HICl_4$, hygroscopic, orange-yellow, compact rhombs, m. p. 45°. *Diethylammonium tetrachloro-iodide*, thin, four-sided, pale yellow plates, m. p. 79° (decomp.). *Ethylenediammonium* bis-*tetrachloro-iodide*, $\left.\begin{matrix}CH_2\cdot NH_2,HICl_4\\ CH_2\cdot NH_2,HICl_4\end{matrix}\right\}2H_2O$, golden-yellow, long, hexagonal prisms,

m. p. 105° (decomp.). *Benzylammonium tetrachloro-iodide*, $C_6H_5{\cdot}CH_2{\cdot}NH_2,HICl_4$, flattened, yellow prisms, m. p. 97° (decomp.). *Dibenzylammonium tetrachloro-iodide*, $(C_6H_5{\cdot}CH_2)_2NH,HICl_4$, fine, yellow needles, m. p. 165°. *Tribenzylammonium tetrachloro-iodide*, $(C_6H_5{\cdot}CH_2)_3N,HICl_4$, yellow rhombs, m. p. 100° (decomp.).
F. G. W.

The Constitution of Galegine. G. Barger and F. D. White (*Biochem. J.*, 1923, **17**, 827—835).—The unsaturated amine, $C_5H_{11}N$, first obtained by Tanret by hydrolysis of galegine from the seeds of *Galega officinalis* (A., 1914, i, 721), gives Hofmann's carbylamine reaction, forms a toluenesulphonamide soluble in sodium hydroxide, and decolorises acid potassium permanganate. It has d_{18}^{18} 0·779, and forms a *chloroplatinate*, m. p. 194—197°, a *chloroaurate*, m. p. 81°, and a *picrate*, m. p. 138·5—139·5°. It is identified as an aminoamylene. The urea obtained by Tanret from galegine arises from a guanidine residue. Galegine sulphate gives Weyl's reaction and the diacetyl reaction, and in the presence of a palladium catalyst takes up 1 mol. of hydrogen to give *dihydrogalegine sulphate*, $(C_6H_{15}N_3)_2,H_2SO_4$, colourless prisms, m. p. 270°. The *nitrate*, long needles, m. p. 75—76°, and the *picrate*, long, narrow plates, m. p. 172°, are also described. On distilling the sulphate with quicklime *iso*amylamine was obtained. Dihydrogalegine (*iso*amylguanidine) synthesised from cyanamide and *iso*amylamine gave the same salts as the product obtained by reduction of galegine from natural sources. The oxidation of galegine sulphate with barium permanganate yielded acetone and glycocyamine. On being boiled with dilute sulphuric acid, galegine takes up 1 mol. of water to form *hydroxydihydrogalegine sulphate*, $(C_6H_{15}ON_3)_2,H_2SO_4$, m. p. 205—206°, which yields on hydrolysis hydroxy*iso*amylamine. *Hydroxydihydrogalegine picrate*, rhomb-shaped crystals, has m. p. 153—154°. On the basis of these results, the formula $Me_2C{:}CH{\cdot}CH_2{\cdot}NH{\cdot}C({:}NH){\cdot}NH_2$ or

$$CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C({:}NH){\cdot}NH_2$$

is ascribed to galegine. The cyclic structures suggested by Tanret (*loc. cit.*) are therefore both incorrect. J. P.

The Absorption Spectra of some Amino-acids. The Possible Ring Structure of Cystine. F. W. Ward (*Biochem. J.*, 1923, **17**, 898—902).—Phenylalanine, tryptophane, and tyrosine show marked absorption bands, whereas alanine, histidine, glutamic acid, and cystine give general absorption. Cystine is the only amino-acid having any marked absorption in the region of the solar ultra-violet, and it shows absorption of greater intensity than that of the other aliphatic amino-acids examined, this being as strong as that of phenylalanine. A possible cyclic structure for cystine is suggested. J. P.

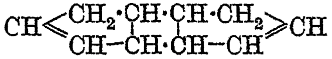
The Reaction between Nitriles and Organo-magnesium Compounds. Ethyl Cyanoacetate. R. Breckpot (*Bull. Soc. chim. Belg.*, 1923, **32**, 386—397).—The yield of ketone obtained from the reaction product of nitriles and the Grignard reagent is practically nil in the case of acetonitrile and phenylacetonitrile. Bruylants (A., 1923, i, 310) postulates the existence of an equilibrium between the tautomeric forms of a nitrile $\colon CH\cdot CN \rightleftharpoons \colon C\colon C\colon NH$, the normal form yielding a ketone by the Blaise reaction, the pseudo-acid form, on the other hand, yielding only condensation products. The formation of the condensation products is the result of the intermediate production of the derivative $\colon C\colon C\colon NMgBr$. With ethyl cyanoacetate and ethyl magnesium bromide, a violent reaction takes place; a certain amount of the ketone is obtained, but the main portion of the reaction mixture consists of tarry products, whilst considerable quantities of gas (ethylene) are evolved. Using four molecular proportions of the Grignard reagent to one of ester, the amount of ethylene obtained shows that the ester contains two labile hydrogen atoms which are almost completely eliminated by the Grignard reagent. If the operation is carried out by adding the Grignard reagent to the nitrile, much ethylene is liberated until slightly more than one gram-molecular proportion has been added, when the reaction stops abruptly, owing to the formation of $CN\cdot CH(MgBr)\cdot CO_2Et$. Addition of water to this compound regenerates the nitrile. The *ketimine* of ethyl propionylacetate, $CH_3\cdot CH_2\cdot C(\colon NH)\cdot CH_2\cdot CO_2Et$, b. p. 100—103°/12 mm., is a colourless liquid of musty odour, d_4^{20} 1·0169, n_D^{20} 1·4938. F. G. P.

The Relation between the Structure of Organic Halides and the Speed of their Reaction with Inorganic Iodides. I. The Problem of Alternating Polarity in Chain Compounds. J. B. Conant and W. R. Kerner (*J. Amer. Chem. Soc.*, 1924, **46**, 232—252).—A method has been developed for comparing the reactivities of the halogen atoms in organic compounds, consisting in measuring the rate of reaction between the organic halide and potassium iodide in acetone solution. The reactivity of the chlorine atom in three series of compounds of the type $A(CH_2)_nCl$ has been measured and compared with the reactivity of the chlorine atom in *n*-butyl chloride. The halogen atom is more reactive in the compounds $A\cdot CH_2Cl$ than in ACl or $A\cdot CH_2\cdot CH_2Cl$ in the three series studied, in which A is either benzoyl, phenyl, or carbethoxy. The influence of the group on the chlorine atom in the compounds of the type $A\cdot CH_2Cl$ is roughly proportional to the effect of the same group on the activity of the hydrogen atom in the compounds of the type $A\cdot CH_3$. In the benzoyl series, the compound $A\cdot CH_2\cdot CH_2Cl$ is eighty times more reactive than a simple normal alkyl chloride; in the phenyl and carbethoxy series, the activity of the corresponding compound is of the same order as that of the alkyl chlorides. The compounds $A\cdot CH_2\cdot CH_2\cdot CH_2Cl$ in the benzoyl and phenyl series are more reactive than the compounds $A\cdot CH_2\cdot CH_2Cl$, this increase being large in the benzoyl series; in the carbethoxy series no such increase is apparent. The chlorine atom in the next higher homologue in the phenyl and carbethoxy series is only as reactive as that in butyl chloride; no higher homologues were available in the benzoyl series. Phenylamyl, phenylhexyl, and phenylheptyl chlorides do not differ significantly in their reactivity from one another or from *n*-butyl or *n*-amyl chlorides.

The preparation and properties of the following compounds are described: β-chloropropiophenone, from β-chloropropionyl chloride and benzene in presence of aluminium chloride, m. p. 49—50° (previous investigators have given it as 57—58°). *γ-Chlorobutyrophenone*, m. p. 19—20°. β-Phenylethyl chloride, from the corresponding alcohol and fuming hydrochloric acid at 140° for four to five hours, b. p. 68·5—69°/4 mm. *Phenylpropyl chloride*, from phenylpropyl alcohol and concentrated hydrochloric acid at 100°, b. p. 85—87°/9 mm. *δ-Phenylbutyl chloride*, b. p. 100—101°/6 mm. *ε-Phenylamyl chloride*, b. p. 111—112°/6 mm. *ζ-Phenylhexyl chloride*, b. p. 115—116°/4 mm. *Phenylheptyl chloride* was obtained only about 88% pure, from the crude alcohol and hydrochloric acid, b. p. 120—140°/3 mm. F. A. M.

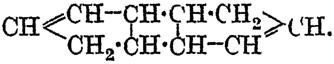
Absorption of Ultra-violet Light by Organic Compounds. II. L. Marchlewski and A. Moroz (*Bull. Soc. chim.*, 1924, [iv], **35**, 37—40).—The results of studying the ultra-violet absorption spectra of alcoholic solutions of nitrobenzene, azoxybenzene, azobenzene, hydrazobenzene, and aniline are given in tables and curves. The extinction coefficients are calculated (cf. this vol., A., ii, 7). E. E. T.

The Constitution of Di*cyclo*pentadiene. H. Staudinger and A. Rheiner (*Helv. Chim. Acta*, 1924, **7**, 23—31).—Commercial di*cyclo*pentadiene can be separated by fractional distillation at a low pressure into two isomerides; the higher-boiling fraction, the β-form, has m. p. 19·5°, whilst the α-form, the known di*cyclo*pentadiene, has m. p. 32·5°. These two forms probably correspond with the formulæ



$$CH<\begin{matrix}CH_2\cdot CH\cdot CH\cdot CH_2\\ CH-CH\cdot CH-CH\end{matrix}>CH$$

and



$$CH<\begin{matrix}CH-CH\cdot CH\cdot CH_2\\ CH_2\cdot CH\cdot CH-CH\end{matrix}>CH.$$

Each of these isomerides should exist in two stereoisomeric forms. The two isomerides which were isolated cannot be stereoisomerides, since by partial reduction they both give the same *dihydrodi*cyclo*pentadiene*, white crystals, m. p. 57°. This compound can be distilled at atmospheric pressure (b. p. 183·5—184·5°) and is therefore more stable than di*cyclo*pentadiene, which, under these conditions, is completely depolymerised. Dihydrodi*cyclo*pentadiene is decomposed into *cyclo*pentadiene and *cyclo*pentene when its vapour is passed over a red-hot platinum spiral. Further reduction of dihydrodi*cyclo*pentadiene gives the known tetrahydrodi*cyclo*pentadiene, which is still more stable, and is with difficulty decomposed to *cyclo*pentene. The disruption of the *cyclo*butane ring in di*cyclo*pentadiene is attributed to the influence of the double bond in the β-position to the carbon linking. A similar cause is responsible for the ready decomposition of limonene, caoutchouc, and hexaphenylethane. *Tri*cyclo*pentadiene* is obtained when di*cyclo*pentadiene is heated in a sealed tube at 170° for some hours. It forms colourless crystals, m. p. 60°, b. p. 90—92°/0·06 mm. It is more stable to heat than di*cyclo*pentadiene or *tetra*cyclo*pentadiene*. The latter is obtained by heating di*cyclo*pentadiene for a longer time at 180°. It has m. p. 188—190°, and when heated at 180—200° decomposes smoothly into *cyclo*pentadiene. When reduced with hydrogen and platinum black, it gives *tetrahydrotetra*cyclo*pentadiene*, m. p. 200—202°, which can be distilled unchanged. Still further polymerisation of di*cyclo*pentadiene results in the production of *poly*cyclo*pentadiene*, an insoluble, infusible, white, crystalline powder, decomposing at 285°. E. H. R.

The Constitution of the Disulphoxides. I. S. SMILES and D. T. GIBSON (*J. Chem. Soc.*, 1924, **125**, 176—183).—The various formulæ given to the disulphoxides at different times are discussed, and an attempt is made to decide between the symmetrical and unsymmetrical formulæ, $R\cdot SO_2\cdot SR$ and $R\cdot SO\cdot SO\cdot R$. Considered as a whole, the evidence at present available favours the unsymmetrical type. The reaction of mercaptans with disulphoxides is studied, and using a mercaptan $R'\cdot SH$, where R' is different from the group R in the disulphoxide it is found that high yields of the sulphinic acid, $R\cdot SO_2H$, are obtained with a mixed disulphide, $R'S\cdot SR$, but no sulphinic acid, $R'\cdot SO_2H$. 2 : 5-*Dichlorobenzenesulphinic acid*, $C_6H_3Cl_2\cdot SO_2H$, forms crystals, m. p. 122°. 2 : 5 : 2′ : 5′-*Tetrachlorodiphenyl disulphoxide*, $(C_6H_3Cl_2)_2S_2O_2$, crystallises in needles, m. p. 128°; 3 : 3′-*dicarboxydiphenyl disulphoxide*, $(C_6H_4\cdot CO_2H)_2S_2O_2$, has m. p. 229°; 2 : 5-*dichloro*-4′-*methyldiphenyl disulphide* forms needles, m. p. 71—72°; *phenyl*-2-*naphthyl disulphide*, m. p. 74—75°; 2 : 5-*dichloro*-3′-*nitrodiphenyl disulphide*, needles, m. p. 89—91°; 9-*anthryl*-4-*tolyl disulphide*, bright yellow needles, m. p. 98—99°; 3-*carboxyphenyl*-4-*tolyl disulphide*, crystals, m. p. 140°. F. G. P.

Preparation of Diphenyl. C. H. LOWE and C. JAMES (*J. Amer. Chem Soc.*, 1923, **45**, 2666—2669).—When using the apparatus previously described (*J. Amer. Chem. Soc.*, 1917, **39**, 933) for the preparation of diphenyl, difficulties arise owing to local heating and sagging of the filament of the heating element, with resulting short-circuiting. A filament support is now described in which these defects are eliminated. It is claimed that by maintaining the filament at a yellowish-red heat very good yields of diphenyl may be obtained from commercially pure benzene, which need not be anhydrous. The addition of more water does not hasten the reaction. W. S. N.

Anthracenemonosulphonic Acids. Sulphonation of Hydrocarbons in a Basic or Neutral Medium. M. BATTEGAY and P. BRANDT (*Bull. Soc. chim.*, 1923, **33**, [iv], 1667—1678; cf. A., 1922, i, 1001).—In the direct sulphonation of anthracene by means of fuming sulphuric acid or chlorosulphonic acid, the separation of the two isomeric anthracenemonosulphonic acids is effected by means of the barium in preference to the sodium salts. The position of the entering sulphonic group was determined by conversion of the acids into the corresponding α- and β-chloroanthraquinones under the influence of nascent chlorine. The two acids are formed in almost equal proportions; elevation of temperature does not appear to favour a greater production of the β-isomeride, as in the case of naphthalene (Fierz and Weissenbach, A., 1920, i, 430), although accurate observation is difficult by reason of the disulphonation of anthracene at temperatures above 100°. When, however, anthracene-α-sulphonic acid was heated in 96% sulphuric acid at temperatures ranging from 150—180° and subsequently transformed into dichloroanthraquinone, the product appeared to consist wholly of the 1 : 5- and 1 : 8-isomerides, thus indicating that no shifting of the sulphonic group from the α- to the β-position had occurred. Sulphonation in presence of mercury, mercurous sulphate, or mercurous oxide resulted in a slight increase in yield without any appreciable effect on the relative proportions of the isomerides. Attempts at sulphonation in a neutral or basic medium (cf. Battegay and Brandt, A., 1922, i, 1001) were made, pyridine being used as the medium in place of the acetic acid employed in the work described above. Experiments were carried out over a temperature range of 95—115° and with varying proportions of the solvent. The best yields were obtained when a portion of the pyridine was replaced by a neutral solvent of higher b. p. In the presence of petroleum at 165—175°, almost the whole of the resulting anthracenesulphonic acid is the α-isomeride, and the addition of mercury compounds has no appreciable influence on the yield or the course of the reaction. When nitrobenzene is used, the yield is considerably smaller. A brief note on the application of Wagner's theory (A., 1886, 708) to the mechanism of the reaction is appended.

Anthracene-α-sulphonic chloride, m. p. 90°, was prepared, but probably in an impure condition; on being heated with alcoholic ammonia, it yields the corresponding *sulphonamide*, brown crystals, m. p. 205° (cf. Heffter, A., 1895, i, 671). H. J. E.

Reactions of Strongly Electropositive Metals with Organic Substances in Liquid Ammonia Solution. IV. Action of the Alkali Metals on Triphenylmethyl and its Compounds. C. A. Kraus and T. Kawamura (*J. Amer. Chem. Soc.*, 1923, **45**, 2756—2763).—The strongly electropositive metals react with triphenylmethyl chloride in liquid ammonia forming the compound of the metal with the triphenylmethyl group, *e.g.*, $CPh_3{\cdot}Na$. The *sodium* compound has been obtained in red needles. With ammonium chloride in liquid ammonia the sodium derivative gives an immediate pink precipitate which turns white on standing owing to production of triphenylmethane, $CPh_3{\cdot}Na \longrightarrow CPh_3{\cdot}NH_4 \longrightarrow CPh_3H + NH_3$. The sodium compound is unstable, but the *potassium* derivative is stable even at 100°. Triphenylmethyl is obtained by the action of triphenylmethyl chloride on sodium triphenylmethyl in the presence of toluene; this reaction does not take place if the sodium compound is replaced by the potassium derivative. Bromobenzene converts sodium triphenylmethyl into tetraphenylmethane. The mechanism of the reduction of organic halides by means of the alkali metals in liquid ammonia solution is discussed. F. G. P.

The Preparation and Properties of Organic Stannichlorides. VI. The Action of Sulphuric Acid on certain Stannichlorides. The Formation of Stannisulphates. J. G. F. Druce (*Chem. News*, 1924, **128**, 33—34; cf. A., 1922, i, 1206).—Stannisulphates of some organic bases can be obtained by the action of concentrated sulphuric acid on the corresponding stannichloride. The stannisulphate crystallises from the sulphuric acid after the addition of ether. *Aniline stannisulphate*, $(PhNH_2)_2,H_2Sn(SO_4)_3$, forms grey, deliquescent crystals. m-*Phenylenediamine stannisulphate*,

$$C_6H_4(NH_2)_2,H_2Sn(SO_4)_3,$$

does not melt below 300°. *Quinoline stannisulphate*,

$$(C_9H_7N)_2,H_2Sn(SO_4)_3,$$

forms colourless, deliquescent needles, m. p. 124°. Potassium and calcium stannisulphates can be prepared in the same way from the stannichlorides. E. H. R.

The Mechanism of the Hofmann Rearrangement of Methylaniline Hydrochloride. J. W. Howard and C. G. Derick (*J. Amer. Chem. Soc.*, 1924, **46**, 166—177).—The investigation was undertaken to confirm Hofmann's original views as to the nature of the change (*Ber.*, 1871, **4**, 742). It was found that in the rearrangement methyl chloride dissociates from the methylaniline hydrochloride and combines with a second molecule, forming phenyltrimethylammonium chloride; this compound then undergoes rearrangement. No rearrangement takes place at 220—250° unless the heating is continued for ninety-six hours. At 300°, however, rearrangement takes place, and is somewhat affected by time, but temperature is the chief factor. Neither methylaniline nor dimethylaniline rearranges. A quantitative separation and determination of the three classes of amine by means of benzenesulphonyl chloride has been worked out. F. A. M.

***p*-Bromophenyltrimethylammonium Perhalides.** T. H. Reade (*J. Chem. Soc.*, 1924, **125**, 148—157; cf. T., 1923, **123**, 141).—The degradation of perhalides by acetone has yielded analogous quaternary ammonium salts in the case of this series, the corresponding *p*-iodo series, and the simple phenyltrimethylammonium series itself, the part removed by acetone being either iodine chloride or bromide or chlorine. The points of difference between the *p*-bromo-series and the unsubstituted series are that *p*-bromophenyltrimethylammonium bromide di-iodide yielded the *p*-bromophenyltrimethylammonium bromide on treatment with acetone, whereas its analogue in the unsubstituted phenyl series was not attacked, and that well-defined double perhalides have been obtained in several reactions. Chlorine replaces *N*-halogen in iodides and periodides, replaces *N*-bromine only when iodine is also present, and replaces added halogens in perbromides. Both bromine and iodine replace *N*-chlorine to an appreciable extent, and iodine replaces *N*-bromine in one instance. p-*Bromophenyltrimethylammonium methyl sulphate*, $C_6H_4Br{\cdot}NMe_3{\cdot}SO_4Me$, white crystals, m. p. 208°, when treated with bromine in hydrobromic acid solution, gives the *perbromide*, $C_6H_4Br\cdot NMe_3Br_3$, orange-red leaflets, m. p. 175°. When warmed with acetone this perbromide yields the *bromide*, $C_6H_4Br\cdot NMe_3Br$, m. p. 210°. Iodine in acetic acid gave $C_6H_4Br\cdot NMe_3Br,IBr$; chlorine similarly yielded

$$C_6H_4Br\cdot NMe_3Br\cdot Cl_2,$$

lemon-yellow plates, m. p. 158°. The bromo-dichloride, the perbromide, and the bromodi-iodide are obtained by the action of halogens on the simple bromide of m. p. 210°. Chlorine with the *p*-bromophenyltrimethylammonium iodide gives the *chloride iodotrichloride*, $C_6H_4Br\cdot NMe_3Cl,ICl_3$, m. p. 187°, bromine gives the *bromoiodobromide*, m. p. 185°, iodine the *tri-iodide*, m. p. 172°. The *chloride iodochloride*, $C_6H_4Br\cdot NMe_3Cl,ICl$, m. p. 177°, is obtained by the action of chlorine on the simple iodide, and on treatment with bromine gives a yellow double perhalide,

$$C_6H_4Br\cdot NMe_3Cl,ICl+C_6H_4Br\cdot NMe_3Br,ICl.$$

Acetone converts the chloride iodochloride into the simple *chloride*, m. p. 199°; this with iodine gives the double compound, $C_6H_4Br\cdot NMe_3I_3 + C_6H_4Br\cdot NMe_3I_5$. The *bromide iodobromide*, $C_6H_4Br\cdot NMe_3Br,IBr$, obtained by the action of bromine on the iodide, crystallises in orange plates, m. p. 189° (decomp.). With chlorine, it yields $C_6H_4Br\cdot NMe_3Cl,ICl_3$; bromine has no action, iodine gives a red double perhalide, $C_6H_4Br\cdot NMe_3Br,IBr+C_6H_4Br\cdot NMe_3BrI_2$. The *bromide di-iodide*, $C_6H_4Br\cdot NMe_3BrI_2$, obtained by the action of iodine on the bromide, has m. p. 172° (decomp.). With chlorine, it yields yellow needles of

$$C_6H_4Br\cdot NMe_3Cl,ICl_3,$$

m. p. 186°, with bromine, the *bromide iodobromide*, m. p. 189°, and with iodine the tri-iodide. The *bromide iodochloride*, $C_6H_4Br\cdot NMe_3Br,ICl$, is obtained by the action of iodine monochloride on the bromide, in the form of yellow crystals, m. p. 178—179°. With chlorine, it yields $C_6H_4Br\cdot NMe_3Cl,ICl_3$, m. p. 186°; with bromine a mixture of the bromide iodobromide and bromide iodochloride, and with iodine a mixture of bromide di-iodide and bromide iodochloride. The *bromide dichloride*, $C_6H_4Br\cdot NMe_3Br,Cl_2$, results by the action of chlorine on the bromide. It forms greenish-yellow crystals, m. p. 158°. Neither chlorine nor bromine has any action on it; with iodine, it yields the *bromide iodochloride*, m. p. 178°. F. G. P.

p-Iodophenyltrimethylammonium Perhalides. T. H. READE and S. A. SIM (*J. Chem. Soc.*, 1924, **125**, 157—160).—Chlorine converts *p*-iodophenyltrimethylammonium iodide into the chloride iodotrichloride, $C_6H_4INMe_3Cl\cdot ICl_3$, and this can be degraded by ethyl malonate, yielding the dichloro-iodide, $C_6H_4I\cdot NMe_3Cl\cdot ICl$. With hot glacial acetic acid, the dichloro-iodide yields a double perhalide, $C_6H_4I\cdot NMe_3Cl_2I+C_6H_4I\cdot NMe_3ClI_2$. p-*Iodophenyltrimethylammonium chloride iodotrichloride*,

$$C_6H_4I\cdot NMe_3Cl\cdot ICl_3,$$

crystallises in yellow needles, m. p. 187°; on treatment with ethyl malonate under reduced pressure it gives the *chloride–iodochloride*, yellow crystals, m. p. 184°. The *tri-iodide* crystallises in brown leaflets, m. p. 189°. A method for determining the ionisable halogen in the perhalides is given. F. G. P.

Synthesis of Indanylamine and of its *N*-Substituted Derivatives. C. Courtot and A. Dondelinger (*Compt. rend.*, 1924, **178**, 493—495; cf. A., 1923, i, 1090).—1-Chloroindane is converted by dry liquid ammonia in a closed vessel, at the ordinary temperature, into 1-indanylamine, b. p. 96—97°/8 mm., and a little di-indanylamine, m. p. 84—85°. Methyl-, dimethyl-, ethyl- and diethyl-amines similarly convert chloroindane into *methylindanylamine*, b. p. 106—107°/15 mm., *dimethylindanylamine*, b. p.1 00°/10 mm., *ethylindanylamine*, b. p. 106—107°/7 mm., and *diethylindanylamine*, b. p. 112—113°/8 mm., respectively, all four amines being colourless liquids.

Indene, on hydrogenation in presence of platinum black, affords indane (in 97% yield), which does not react with magnesium ethyl bromide at 135° (cf. Grignard and Courtot, A., 1911, i, 193). The reactivity of the methylene group in indene is therefore due to the presence of unsaturation in the 5-membered ring. E. E. T.

Preparation of 3 : 3′-Diaminodiphenylsulphone by Electrolytic Reduction of 3 : 3′-Dinitrodiphenylsulphone. J. Lacroix (*Compt. rend.*, 1924, **178**, 483—486).—The electrolytic reduction of 3 : 3′-dinitrodiphenylsulphone to the diamino-derivative is best effected (yield, 94·5%) by the use of an alcoholic solution of the dinitro-compound acidified wth hydrochloric acid as the cathode liquid, with a cathode consisting of nickel foil covered with spongy tin. The anode is of lead immersed in 10% sulphuric acid. The cathode liquid is maintained at a temperature of 68—72° and well agitated. A. B. H.

Chloronitrobenzenes and Thiocarbamides. J. Taylor and A. E. Dixon (*J. Chem. Soc.*, 1924, **125**, 243—250).—Neither *o*- nor *p*-chloronitrobenzene nor 2 : 5-dichloronitrobenzene combines with thiocarbamide. 1-Chloro-2 : 4-dinitrobenzene unites with thiocarbamide and with phenylthiocarbamide to form additive salts, from which alkali hydroxides eliminate hydrogen chloride, the dinitrophenyl residue breaking off as dinitrophenyl mercaptan. With thiocarbanilide, chlorodinitrobenzene gives mainly phenylthiocarbimide and dinitrodiphenylamine, $(NO_2)_2C_6H_3$·NHPh. Picryl chloride unites with thiocarbamide to form an *additive* compound, from which a *picrate* and a *salicylate* were obtained. Phenylthiocarbamide gave little additive salt, thiocarbanilide none. The picryl compounds are unstable, decomposing readily into dipicryl sulphide and a dark-coloured powder. In no case was an *N*-substituted thiocarbamide obtained, the behaviour of dinitrochlorobenzene and picryl chloride thus more resembling that of an alkyl halide than of an acid chloride. The *picrates* of the compounds obtained from 1-chloro-2 : 4-dinitrobenzene with thiocarbamide and phenylthiocarbamide are yellow compounds, m. p. 192—193° and 160—161°, respectively. The *picrate* derived from picryl chloride and thiocarbamide has m. p. 149—150°, the *salicylate*, m. p. 76°. F. G. P.

The Decomposition of Substituted Carbamyl Chlorides by Hydroxy-compounds. I. The Reaction between Phenylmethylcarbamyl Chloride and Ethyl Alcohol at Different Temperatures. T. W. PRICE (*J. Chem. Soc.*, 1924, **125**, 115—129).—The reaction between phenylmethylcarbamyl chloride (m. p. 87·5°) and alcohol is very slow at temperatures below the boiling point of alcohol, and was consequently studied in sealed tubes at 100°, 90°, 80°, and 70°. Under these conditions, the carbamyl chloride first reacts with the alcohol to form phenylmethylurethane together with hydrogen chloride, which then reacts further with alcohol to form ethyl chloride and water. The first reaction was studied separately by adding dimethylaniline to the reaction mixture to combine with the hydrogen chloride and prevent the formation of ethyl chloride. The velocity of the reaction between the alcohol and the carbamyl chloride was found to vary with the amount of dimethylaniline added, being slower in presence of more base. Three series of experiments were therefore made at 100° with different amounts of dimethylaniline, and the velocity constant of the reaction in absence of dimethylaniline was found by extrapolation to be $k_1=0{\cdot}0426$ at 100°. As this value was in good agreement with the value obtained by calculation from the study of the combined reaction, measurements in presence of varying quantities of dimethylaniline were omitted at the other temperatures. The position of the reaction under these conditions was determined by titration of the dimethylaniline hydrochloride present at any given moment, the initial concentration of the carbamyl chloride in the alcohol being in all cases $N/2$. The action of hydrogen chloride ($N/2$) on ethyl alcohol was investigated separately. The velocity constant fell steadily at each temperature, the means of the first three values being $k_2 = 0{\cdot}0102$ at 100°, 0·00443 at 90°, 0·00162 at 80°, and 0·000521 at 70°.

The whole reaction was then studied by determining the amounts of carbamyl chloride, hydrogen chloride, and ethyl chloride present at any instant. The hydrogen chloride was determined by direct titration, and the carbamyl chloride by hydrolysis with excess of potassium hydroxide after removal of the ethyl chloride, followed by titration with silver nitrate. The velocity constants of the first reaction, calculated from the amounts of carbamyl chloride present, were $k_1=0{\cdot}0427$ at 100°, 0·0196 at 90°, 0·00873 at 80°, and 0·00329 at 70°. Expressions deduced for the amounts of the various reactants present at any time from the values of k_1 and k_2, as well as for the maximum amount of hydrogen chloride present and the time taken for this maximum to be reached, gave satisfactory agreement with experimental results, and the variation of temperature coefficient for each reaction was shown to be in accordance with Lewis' deductions. F. G. W.

Esterification of *cyclo*Hexanol and of some of its Homologues. (MLLE.) G. CAUQUIL (*Compt. rend.*, 1924, **178**, 323—326).—*cyclo*Hexanol, 2-methyl*cyclo*hexanol, or 3 : 4-dimethyl*cyclo*hexanol was heated, at 95°, with an equivalent weight of acetic acid until equilibrium was attained, when it was found that 55·6%, 49·8%, and 47·5% of the three alcohols, respectively, had undergone esterification. E. E. T.

The Catalytic Hydrogenation of Organic Fluoro-derivatives. III. The Hydrogenation of ω-Trifluoro-*m*-cresol. F. SWARTS (*Bull. Soc. chim. Belg.*, 1923, **32**, 367—376; cf. A., 1921, i, 656).—The hydrogenation of ω-trifluoro-*m*-cresol in the presence of platinum black proceeds in two directions, one resulting in the formation of ω-trifluoromethyl*cyclo*hexanol, the other in the production of ω-trifluoromethyl*cyclo*hexane and water, the group CF_3– being unaffected. The relative proportions of the *cyclo*hydrocarbon and *cyclo*alcohol are not constant, increase of temperature favouring the production of the hydrocarbon. In the case of ω-trifluoro-*m*-cresol, a thermal coefficient of acceleration is observed, whilst the velocity of absorption of the hydrogen by the trifluoromethyl*cyclo*hexane varies little with the temperature. An attempt is made to deduce a formula by means of which the thermal coefficient of the reaction can be calculated.

*Trifluoromethyl*cyclo*hexan-3-ol,* $CF_3{\cdot}C_6H_{10}{\cdot}OH$, is a viscous liquid, b. p. 183—184°; its *benzoyl* derivative crystallises in prisms, m. p. 55°, d^{17} 1·2611. The *acetyl* derivative has b. p. 192·5—194°. *Trifluoromethyl*cyclo*hexan-3-one* is obtained by oxidising the corresponding *cyclo*hexane with chromic acid; it boils at 173—174°/746 mm., d^{16} 1·242. Its *semicarbazone* melts at 190°. F. G. P.

The Lead Derivative of Trinitroresorcinol. C. A. TAYLOR and W. H. RINKENBACH (*U.S. Bur. Mines, Repts. Investigations*, 1923, No. 2533).—The *lead* derivative of trinitroresorcinol is obtained in 94·4% yield, as fine, light orange-coloured crystals, *d* 3·09, by mixing boiling solutions of lead nitrate, trinitroresorcinol, and sodium carbonate, to which glacial acetic acid has been added. Its explosion temperature is 293° and rate of detonation 2097—2209 m. per second. CHEMICAL ABSTRACTS.

The Influence of Hydrogen Concentration on the Autoxidation of Quinol. A Note on the Stability of the Quinhydrone Electrode. V. K. LAMER and E. K. RIDEAL (*J. Amer. Chem. Soc.*, 1924, **46**, 223—231).—The rate at which quinol reacts with molecular oxygen has been followed by shaking borate buffers, $0{\cdot}01M$ with respect to quinol, with oxygen. The rate does not become appreciable until the solution is more alkaline than p_H 7·3 or 7·8 for air. The rate of reaction is highly sensitive to further increase of p_H value, being proportional to $[H^+]^{3/2}$, where $[H^+]$ is the hydrogen-ion concentration, for the region investigated. A mechanism involving complex formation of the primary and secondary ions is suggested to explain this relationship, such as: $2H_2C_6H_4O_2 \longrightarrow 3H^+ + HC_6H_4O^- + C_6H_4O^= \longrightarrow$ complex ion; complex$+2O_2 \longrightarrow 2$ quinone$+H_2O_2$. F. A. M.

Arylazides. III. Quinol Ethers from *p*-Methylated Arylazides. E. BAMBERGER and J. BRUN (*Helv. Chim. Acta*, 1924, **7**, 112—122).—A detailed account of experiments the results of which have already been recorded (A., 1921, i, 721). E. H. R.

Arylazides. IV. Iminoquinol Ethers from *p*-Methylated Arylazides. E. BAMBERGER, J. BRUN, and A. HARTMANN (*Helv. Chim. Acta*, 1924, 7, 123—131).—A detailed account of work already published (A., 1921, i, 721). E. H. R.

Electrochemical Oxidation of Alkyl Ethers of Phenol and of the Three Isomeric Dihydroxybenzenes. F. FICHTER and W. DIETRICH (*Helv. Chim. Acta*, 1924, 7, 131—143).—Anodic oxidation of anisole in suspension in dilute sulphuric acid, using a lead peroxide anode, results in a high yield of benzoquinone, up to 71% of theory under favourable conditions. This result is obtained using a diaphragm; in absence of a diaphragm, a mixture of quinhydrone and quinol is obtained. Quinol monomethyl ether is probably formed as an intermediate product, since this is converted practically quantitatively into benzoquinone by anodic oxidation. The methyl group is oxidised to methyl alcohol. When a platinum anode is used the yield of benzoquinone is very small; some formaldehyde is formed but the principal product is carbon dioxide. Phenetole and phenyl *iso*amyl ether give smaller yields of benzoquinone, whilst the alkyl group is in each case oxidised to the corresponding acid. Quinol dimethyl ether gives benzoquinone, the best yield being 48·6% of theory.

By the oxidation of guaiacol, using a diaphragm, at first only fumaric acid could be obtained; this, in absence of a diaphragm, was reduced to succinic acid. By stopping the oxidation at an early stage, however, an oily product was obtained from which a diphenyl derivative, *diguaiacol*, was isolated. This is probably 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxydiphenyl*; it crystallises in slender needles, m. p. 166°, and gives an orange colour with ferric chloride. Its *diacetyl* derivative crystallises in leaflets, m. p. 198°, and its *dibenzoyl* derivative in white needles, m. p. 203°. By demethylation, it gives a *tetrahydroxydiphenyl* (? 3 : 4 : 3′ : 4′), needles, m. p. 134°, giving an emerald-green coloration with ferric chloride. Its *tetra-acetyl* derivative has m. p. 161°. Further methylation of diguaiacol converts it into *diveratrole*, or *tetramethoxydiphenyl*, colourless tablets or leaflets, m. p. 130°. Anodic oxidation of veratrole gives rise to some diveratrole, but in addition, partial demethylation occurs with formation of a *hydroxytrimethoxydiphenyl*, which gives an *acetyl* derivative, pale yellow leaflets, m. p. 116°. Anodic oxidation of resorcinol monomethyl ether gives an amorphous *dihydroxydimethoxydiphenyl* which, when demethylated, gives 2 : 4 : 2′ : 4′-tetrahydroxydiphenyl (2 : 4 : 2′ : 4′-diresorcinol). E. H. R.

The Catalytic Condensation of Acetylene with Phenols. H. H. WENZKE and J. A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1924, 46, 177—181).—Acetylene condenses with phenols and cresols in 95% alcoholic solution, in presence of sulphuric acid and mercury salts, to form uncrystallisable resins. The di- and trihydroxybenzenes react even more readily. With β-naphthol, acetylene condenses to form an acetal and some ethylidenedi-β-naphthol. Resorcinol condenses with acetylene to form ethylidenediresorcinol (as-2 : 4 : 2′ : 4′-*tetrahydroxydiphenylethane*), which loses water spontaneously to form 3 : 6-*dihydroxy-9-methylxanthene*, soluble in water and alkalis (decomp. 230—240°). On heating with stannic chloride at 160—180°, it oxidises to form 6-*hydroxy-9-methylfluorone*, the solutions of which resemble that of fluorescein.

The presence of nitro- and sulphonic groups prevents the absorption of acetylene by a phenolic compound. No cases have been noted where the acetylene substitutes in a meta-position to another group. Phenetole does not react with acetylene under the above conditions. F. A. M.

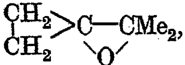
The Hydrobenzoin Rearrangement. I. Hydroanisoin. M. Tiffeneau and A. Orékhoff (*Bull. Soc. chim.*, 1923, **33**, [iv], 1832—1838).—According to Russell (*Annalen*, 1869, **151**, 25), hydroanisoin, on dehydration, affords deoxyanisoin (m. p. 95°). Irvine and Moodie (T., 1907, **91**, 536) found for the latter compound the m. p. 108—109°. It is now shown that Russell's compound is *dianisylacetaldehyde*, $(OMe\cdot C_6H_4)_2CH\cdot CHO$, as would have been expected (cf. Orékhoff and Tiffeneau, A., 1921, i, 566). The aldehyde (needles, m. p. 104—105°; *semicarbazone*, m. p. 140—141°) is also obtained by treating magnesium *p*-anisyl bromide with ethyl ethoxyacetate, and the product of this interaction with formic acid. On oxidation, the aldehyde affords dianisyl ketone, and with magnesium phenyl bromide gives *α-phenyl-*ββ-di-*p-anisylethyl alcohol* (needles, m. p. 139—140°). Hydroanisoin (m. p. 170—171°), on heating with 50% sulphuric acid, affords the above aldehyde, *iso*hydroanisoin (m. p. 125—126°) behaving similarly.

Dianisyl ketone with magnesium methyl iodide is converted into *dianisylethylene*, $(OMe\cdot C_6H_4)_2C{:}CH_2$ (m. p. 142—143°), the latter, when treated with mercuric oxide in presence of water and iodine, affording an iodohydrin (not isolated) which is converted by silver nitrate into deoxyanisoin. E. E. T.

Semi-pinacolic Transformation. Necessity for the Presence of the Phenyl Group in Semi-pinacolic Transformations. (Mlle.) J. Lévy (*Bull. Soc. chim.*, 1923, **33**, [iv], 1655—1666; cf. Tiffeneau and Lévy, A., 1923, i, 788, 789).—In the aromatic series, the stability of the secondary hydroxyl group in respect of semi-pinacolic transformations appears to be conditioned by the nature of the aryl group linked to the secondary carbon atom. The author has studied the dehydration of six tri-substituted glycols and draws the conclusion that in addition to transpositions involving only phenylic groups in which the shifting of a group occurs only when the group capable of migration is arylic, others take place only in the cyclic series, but this is limited to cases in which the aryl group occupies one definite position. In these cases, the migratory group may be either cyclic or acyclic. Experimental details of the dehydration of the glycols are given (cf. A., 1921, i, 860). The following substances are described: βγ-*di-*

hydroxy-α-phenyl-γ-methylbutane, needles, m. p. 64—65°; *ethyl benzylglycollate*, b. p. 170—173°/30 mm.; *benzyl* iso*propyl ketone*, b. p. 234—235°; *semicarbazone*, m. p. 140—141°; *α-phenyl-γ-ethylpentane-βγ-diol*, small needles, m. p. 79—80°, yielding on dehydration by means of sulphuric acid an oil, b. p. 160—170°/50 mm., which forms a semicarbazone, m. p. 160—161°; *αδ-diphenyl-γ-benzylbutane-βγ-diol*, crystals, transformed by concentrated sulphuric acid into a substance, $C_{23}H_{20}$, m. p. 94—95°, of unknown constitution; *α-methylhexane-β-ol*, b. p. 140—142°/760 mm., prepared by the action of magnesium butyl bromide on acetone, yields on dehydration a *methyl-Δ^{β}-hexene*, b. p. 95—98°/760 mm., which on treatment with hypoiodous acid yields an *iodohydrin*; this is converted into a ketone on treatment with silver nitrate without undergoing any transposition. H. J. E.

3 : 4-Dihydroxyphenylmethylaminoethanol (Adrenaline). I. HOSHINO and DAIICHI SEIYAKU KABUSHIKI KAISHA (Japan. Pat. 42351).—Adrenaline is prepared from methylaminoacetyl-3 : 4-dihydroxybenzene by reducing with hydrogen, using as a catalyst colloidal solutions of metals of the platinum group, the finely powdered metals, or nickel or carbon bearing these metals. The product is purer than that obtained by Stolz's method and the yield almost theoretical. K. K.

Cyclic Trimethylene [*cyclo*Propane] Compounds. P. BRUYLANTS (*Bull. Soc. chim. Belg.*, 1923, **32**, 358—367).—Bromination (in direct sunlight) of *cyclo*propane-1-carboxylic chloride, until the liquid boils at 135—140°, followed by treatment of the product with methyl alcohol, gives a mixture of methyl *cyclo*propane-1-carboxylate, *methyl* 1-*bromo*cyclo*propane*-1-*carboxylate* (a colourless, mobile liquid, b. p. 168°/702 mm., d_4^{20} 1·545, n_D^{20} 1·4784), and *methyl αγ-dibromobutyrate*. The latter (b. p. 113—114°/14 mm.) is the only product of bromination in the dark, and was identified by conversion into αγ-dibromobutyramide (m. p. 80—82°). cyclo*Propane*-1-*carboxylic anhydride*, which, on bromination, gives only open-chain derivatives, is a colourless liquid, b. p. 232°/752 mm., d_4^{20} 1·1132, n_D^{20} 1·4628. The corresponding *ethyl* ester has b. p. 178°/758 mm., d_4^{20} 1·428, n_D^{20} 1·4678. The esters are converted by ammonia into the *amide* (needles, m. p. 108°), and by concentrated sodium hydroxide into the *acid*, m. p. 77°. Magnesium methyl bromide converts the methyl ester into the *bromohydrin* (b. p. 171—172°/762 mm.), the latter with acetic anhydride giving the *bromo-acetin* (b. p. 180—182°, d_4^{20} 1·327, n_D^{20} 1·4731), and with alkali hydroxide the *oxide*,  $\left.\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right>C\underset{\diagdown O \diagup}{—}CMe_2$, b. p. 121—125°, d_4^{20} 0·886, n_D^{20} 1·419. Digestion of the oxide with dilute sulphuric acid, followed by addition of semicarbazide, gives a *semicarbazone* (?), m. p. 115—140° (very indefinite). Electrolysis of potassium *cyclo*propanecarboxylate yields the free acid and a little *cyclo*propane.

F. G. P.

Preparation and Properties of some Organic Uranyl Salts and, in particular, of Uranyl Benzoates and Salicylates. G. COURTOIS (*Bull. Soc. chim.*, 1923, **33**, [iv], 1761—1773).—A continuation of previous work (A., 1914, i, 799, 802). When the hydroxide, UO_3,H_2O, is dissolved in a hot aqueous solution of benzoic acid, and the solution evaporated, *uranyl benzoate*, $(Ph{\cdot}CO_2)_2UO_2$ (yellow crystals, stable at 100°), separates, together with benzoic acid, which may be extracted with benzene. On further evaporation, the *acid* salt, $(Ph{\cdot}CO_2)_2UO_2,Ph{\cdot}CO_2H$, separates, the latter salt also being obtained if uranyl hydroxide is dissolved in boiling benzoic acid. Uranyl benzoate is sparingly soluble in water, the solution depositing a basic salt on standing. Below 5°, the saturated aqueous solution deposits the *dihydrate*, which becomes anhydrous on keeping at the ordinary temperature, and dissolves in ether to give a solution which rapidly deposits a yellow, crystalline compound, $(Ph{\cdot}CO_2)_2UO_2,2Et_2O$. The latter is also formed when a concentrated aqueous solution of the benzoate is shaken with ether, and slowly loses ether of crystallisation on keeping (rapidly at 100°).

Uranyl hydroxide dissolves in a hot alcoholic solution of benzoic acid, the *compound*, $(Ph{\cdot}CO_2)_2UO_2,EtOH$ (pale yellow crystals, from which ether displaces the alcohol of crystallisation), separating on cooling. This salt, on crystallisation from water or from chloroform, or on heating at 100°, loses its alcohol of crystallisation.

When aqueous solutions of uranyl benzoate are concentrated by protracted (hot) evaporation, a yellow, crystalline, *basic* salt, $(PhCO_2)_2UO_2,UO_3,H_2O$, separates, and may be freed from accompanying uranyl benzoate by extracting the latter with alcohol. Prolonged heating with water converts the basic salt into uranyl hydroxide.

Aqueous solutions of uranyl benzoate are unaffected by sunlight, whilst alcoholic solutions afford a violet precipitate of uranoso-uranic oxide, the latter becoming yellow on washing with water containing dissolved air.

Uranyl salicylate, $(OH{\cdot}C_6H_4{\cdot}CO_2)_2UO_2$, separates as orange-yellow crystals, readily soluble in methyl or ethyl alcohol, from the warm solution obtained by heating uranyl hydroxide with aqueous salicylic acid. The mother-liquors, on cooling, deposit the *dihydrate* of the above salt in the form of yellow crystals, giving red solutions in methyl or ethyl alcohol and becoming anhydrous at 140—150°, with slight decomposition. Aqueous solutions of uranyl salicylate, on boiling, acquire a red colour. Neither aqueous nor alcoholic solutions of the salt are affected by sunlight, a fact that distinguishes the salt from all other uranyl salts studied. E. E. T.

Stability of Solutions of some Organic Uranyl Salts in Absence or in Presence of Light. G. COURTOIS (*Bull. Soc. chim.*, 1923, **33**, [iv], 1773—1785).—Previous results (A., 1914, i, 799 and 802; and preceding abstract) are re-stated and slightly extended. It is shown that saturated aqueous solutions of the following uranyl salts are unstable even in absence of light, giving crystalline basic salts (already described): Formate, acetate, benzoate, glycollate, and citrate. The other uranyl salts examined (propionate, butyrate, lactate, quinate, salicylate, oxalate, and tartrate) are stable in the dark in aqueous solution.

Sunlight, in absence of air, causes the reduction of all the above salts, with the exception of the benzoate and salicylate. The stability of the latter may be due to the "antioxygen" property of the salicylate residue. Contrary to the view of Aloy and Rodier (A., 1920, ii, 182), decomposition by sunlight does not depend on the hydroxylic character of the salt, as in the case of the tartrate, since uranyl propionate, butyrate, etc., are decomposed in aqueous solution under the influence of sunlight. In these cases, the violet hydrated uranoso-uranic oxide (converted by washing with water into the oxide, $UO_3,2H_2O$), is precipitated. Alcohol (or ether) accelerates these decompositions, but does not initiate them. In the decomposition of uranyl salts of monobasic aliphatic acids, carbon dioxide and a hydrocarbon result (the formate giving carbon monoxide and dioxide). The other salts examined give rise to carbon dioxide, except the oxalate, which also affords the monoxide. In the case of the glycollate (lactate), formic acid and formaldehyde (acetaldehyde) are first formed. E. E. T.

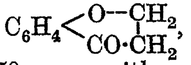
The Isoelectric Point of *m*-Aminobenzoic Acid and its Equilibrium with Water, Acetic Acid, and Sodium Acetate. J. Barbaudy (*Bull. Soc. chim.*, 1924, [iv], **35**, 31—37).—The equilibria in the systems: (1) *m*-aminobenzoic acid, acetic acid, and water, and (2) *m*-aminobenzoic acid, acetic acid, sodium acetate, and water have been studied at 25°, by determinations of hydrogen ion concentration, density, and viscosity in addition to solubility. From the solubility of *m*-aminobenzoic acid in pure water, the p_H of the isoelectric point for this acid is found to be 3·886. System (1) gave concordance between calculated and found isoelectric points, whilst in system (2) concordance was less good. [Cf. Michaelis and Davidsohn, A., 1911, ii, 192.] E. E. T.

Preparation of Benzyl Diphenylalkylacetates and the Corresponding Acids by Means of Sodamide and Alkyl Iodides. (Mme.) P. Ramart (*Compt. rend.*, 1924, **178**, 396—397; cf. this vol., i, 171).—Benzyl diphenylacetate was dissolved in ether and heated with powdered sodamide for several hours, an alkyl halide then being added and so on. The following new compounds (in addition to some previously known) have been prepared by this method: *Benzyl αα-diphenylpropionate*, prisms, m. p. 71—72°, b. p. 230—233°/10 mm.; *benzyl αα-diphenyl-β-methylbutyrate*, m. p. 73—74°, b. p. 225°/2 mm.; *αα-diphenyl-*Δ^{γ}*-pentenoic* acid, prisms, m. p. 142° (*benzyl* ester, b. p. 240—242°/10 mm.; *amide*, m. p. 90—92°). E. E. T.

The Methods of Preparation of 6-Chloro-3-hydroxybenzoic Acid. V. I. Minaev and K. M. Ripper (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 673—679).—A further account of work already published (A., 1922, i, 162). G. A. R. K.

β-Phenoxypropionic Acid and some of its Derivatives. Chromanone. S. G. POWELL (*J. Amer. Chem. Soc.*, 1923, **45**, 2708—2711).—In preparing γ-phenoxypropyl alcohol,

$$Ph\cdot O\cdot[CH_2]_2\cdot CH_2OH,$$

(Rindfusz, A., 1919, i, 342), an aqueous solution of sodium phenoxide, in which trimethylenechlorohydrin is completely soluble, may be used in place of an absolute-alcoholic solution; in fact, a slightly better yield (80%) is actually obtained by this method. β-Phenoxypropionic acid, $Ph\cdot O\cdot[CH_2]_2\cdot CO_2H$, may be obtained in yield varying between 32% and 45% by the gradual addition of potassium permanganate solution to a suspension of β-phenoxypropyl alcohol in a solution of magnesium sulphate. Its *ethyl* ester, a colourless oil, has b. p. 170°/40 mm. The acid *chloride*, a liquid of irritating odour, is obtained when the acid is gently warmed for a few seconds with only a slight excess of thionyl chloride; it reacts with aqueous ammonia, giving the *amide*, glistening needles, m. p. 119°. The action of phosphoric oxide in boiling benzene solution on the acid gives *chromanone*,  $C_6H_4<\begin{matrix}O-CH_2\\ \quad\ \mid\\ CO\cdot CH_2\end{matrix}$, a colourless, highly refracting liquid, b. p. 160°/50 mm., with a pleasant, lemon-like odour; it solidifies on keeping to a mass of crystals, m. p. 38·5°. Chromanone is also formed, together with a fraction of b. p. 237°/50 mm. (which is free from halogen), by the prolonged action of an excess of thionyl chloride on β-phenoxypropionic acid. Chromanone forms an *oxime*, glistening needles, m. p. 140°, and a *benzylidene* derivative, long, yellow needles, m. p. 112°. W. S. N.

The Isomeric Esters of *p*-Methoxybenzoylacrylic Acid. G. P. RICE (*J. Amer. Chem. Soc.*, 1924, **46**, 214—223; cf. A., 1923, i, 218).—In continuation of previous work on the isomeric esters of benzoylacrylic acid, the isomeric methyl and ethyl esters of *p*-methoxybenzoylacrylic acid have been examined. The stable yellow forms when exposed to sunlight in benzene solution are converted into colourless isomerides, the reverse change taking place on exposing solutions of the colourless solids, containing a crystal of iodine, to sunlight. *p*-Methoxybenzoylacrylic acid itself is transformed by sunlight to a polymeric acid. The yellow unsaturated esters are much more readily hydrolysed by sodium carbonate than the colourless isomerides, the product being methoxybenzoylacrylic acid. With cold concentrated or boiling dilute hydrochloric acid, both isomeric esters give a mixture of unsaturated acid and α-hydroxy-*p*-methoxybenzoylacrylic acid.

The esters of the *p*-methoxy-acid do not behave in the same way as the esters of the unsubstituted acid on treatment with semicarbazide. *p*-Methoxybenzoylacrylic acid itself yields a semicarbazone; the colourless esters react with semicarbazide to form additive products and semicarbazones of these additive products.

Methyl p-*methoxybenzoylacrylate*, yellow needles, m. p. 71—72°; *colourless isomeride*, needles, m. p. 62°. *Ethyl* p-*methoxybenzoylacrylate*, large, yellow crystals, m. p. 42—43°, b. p. 210—215°/11 mm.; *colourless isomeride*, m. p. 46—47°. *Methyl* αβ-*dibromo-*

p-*methoxybenzoylpropionate* from the yellow ester, m. p. 115°. *Ethyl* αβ-*dibromo*-p-*methoxybenzoylpropionate* from the yellow ester, 1st isomeride, m. p. 51°; 2nd isomeride, m. p. 66°.

Bromination of *p*-methoxybenzoylacrylic acid yielded two isomeric forms of αβ-*dibromo*-p-*methoxybenzoylpropionic acid*, m. p. 140° and 164°, respectively. The *polymeric acid*, $C_{20}H_{20}O_8$, from *p*-methoxybenzoylacrylic acid, has m. p. 180°.

α-*Hydroxy*-p-*methoxybenzoylacrylic acid* (from hydrolysis of unsaturated acid) has m. p. 122°.

The yellow methyl *p*-methoxybenzoylacrylate reacts with 1 mol. of semicarbazide and yields two isomeric *semicarbazones*, yellow needles, m. p. 165°, and colourless plates, m. p. 178°. The same yellow methyl ester on treatment with two molecular proportions of semicarbazide yields the *semicarbazone* of *methyl* α-*semicarbazido*-p-*methoxybenzoylpropionate*, m. p. 178° (decomp.). *Methyl* α-*semicarbazido*-p-*methoxybenzoylpropionate*, m. p. 161—162°, is obtained as a by-product in preparation of the semicarbazone, m. p. 178°, and also by treating the semicarbazone of methyl α-semicarbazido-*p*-methoxybenzoylpropionate with concentrated hydrochloric acid.

Treatment of the solid, m. p. 161°, with nitrous acid gave *methyl nitroso*-α-*semicarbazido*-p-*methoxybenzoylpropionate*, m. p. 132° (decomp.).

In a similar manner, the yellow ethyl ester of *p*-methoxybenzoylacrylic acid yields two isomeric *semicarbazones*, colourless crystals, m. p. 165°, and yellow crystals, m. p. 124°.

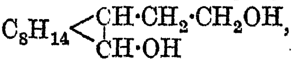
The *semicarbazone* of *ethyl* α-*semicarbazido*-p-*methoxybenzoylpropionate*, m. p. 182° (decomp.), and *ethyl* α-*semicarbazido*-p-*methoxybenzoylpropionate*, m. p. 173°, and the *nitroso*-compound, m. p. 124—125° (decomp.), are described.

Methoxybenzoylacrylic acid itself yields a *semicarbazone*, pale yellow solid, m. p. 216° (decomp.). F. A. M.

Constitution of Phthalonic Acid. CORNILLOT (*Compt. rend.*, 1924, **178**, 490—492).—Phthalonic anhydride is rapidly converted by acetic acid at 100° into the acetyl-ψ-phthalonic acid described by Kuroda and Perkin (T., 1923, **123**, 2094), who concluded that phthalonic acid has the phthalide structure. With this conclusion the author disagrees, since the anhydride possesses the normal structure. Acetyl chloride or acetic anhydride converts phthalonic acid into a mixture of phthalonic anhydride and acetyl-ψ-phthalonic acid, the proportions of the two products varying with the conditions of experiment. In boiling ethyl acetate solution (with acetic anhydride) or in suspension in acetyl chloride, almost pure phthalonic anhydride results, whilst the latter, on boiling for an hour with acetic anhydride, is entirely converted into the acetyl-ψ-acid. In any case (as in the work of Kuroda and Perkin), the secondary reaction is responsible for the production of the acetyl-ψ-acid. [See also Tcherniac, T., 1916, **109**, 1236.] E. E. T.

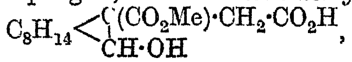
Condensations of Aldehydes with Resorcinol and some other Aromatic Hydroxy Compounds. R. N. SEN and N. N. SINHA (*J. Amer. Chem. Soc.*, 1923, **45**, 2984—2996).—The benzein type of compound has been prepared by condensing aldehydes with resorcinol and similar substances in the presence of concentrated sulphuric acid at 100—130°. The intensity of the fluorescence of alkali solutions of these compounds varies with the number and the position of hydroxyl and carboxyl groups, the influence of hydroxyl groups being greater when they occur in the benzene nuclei associated with the pyrone ring than when they occur in the phenyl residue, whereas the opposite is the case with the carboxyl group. *Resorcinol-1′-hydroxybenzein*, $C_{19}H_{12}O_4$, has m. p. above 260°. Its *tetrabromo*-derivative forms red crystals. *Resorcinol-2′-methoxy-3′-hydroxybenzein*, $C_{20}H_{14}O_5$, is obtained from vanillin and resorcinol as a greyish-black powder, m. p. above 295°. *Gallic acid benzein*, $C_{21}H_{12}O_9$, from gallic acid and benzaldehyde, is a green, microcrystalline powder. *Resorcinolethein*, $C_{14}H_{10}O_3$, from resorcinol and paraldehyde, is a black, microcrystalline powder, m. p. above 290°. *Resorcinolphenetoleazobenzeinsulphonic acid*, $C_{27}H_{20}O_7N_2S$, from phenetoleazobenzaldehydesulphonic acid and resorcinol, does not fluoresce. *Resorcinol*-p-*hydroxybenzein*-m-*carboxylic acid*, $C_{20}H_{12}O_6$, is a yellow powder, m. p. above 295°. β-*Resorcylic acid benzein*, $C_{21}H_{12}O_7$, from β-resorcylic acid and benzaldehyde, is a yellow powder. *Resorcinol-3′-methoxybenzein*, $C_{20}H_{14}O_4$, from anisaldehyde and resorcinol, gives a red *tetrabromo*-derivative, decomposing at 200°. F. G. P.

Reduction Products of some Acids Derived from Camphor. L. PALFRAY (*Ann. Chim.*, 1923, **20**, [ix], 297—385).—A republication of work previously described (A., 1921, i, 418; 1922, i, 548; also Haller and Palfray, A., 1923, i, 577) with additional matter. Reduction of the dimethyl ester of carboxycamphoracetic acid by means of sodium and absolute alcohol resulted in the formation of a mixture of borneol, *camphoracetic glycol*,



$C_8H_{14}<\begin{array}{l}CH\cdot CH_2\cdot CH_2OH\\ |\\ CH\cdot OH\end{array}$,

an oil, b. p. 195—198°/14 mm., α_D^{15} +19° 57′, yielding a *phenylurethane*, colourless spangles, and the *monomethyl* ester,



$$C_8H_{14}<\begin{array}{l}C(CO_2Me)\cdot CH_2\cdot CO_2H\\ |\\ CH\cdot OH\end{array},$$

α_D^{20} +49° 22′. Similar reduction of the diethyl ester also yields borneol, the same glycol, and a substance of the formula $C_{15}H_{23}O_3$, probably a lactone, crystals, m. p. 50—51°, α_D^{14} +62° 22′. A discussion on the molecular refraction of the substances dealt with is appended. The following additional data are given. Ethyl hydrogen camphorate has m. p. 56—56·5°; the diethyl ester of carboxycamphoracetic acid has b. p. 202—204°/18 mm., $d_4^{24\cdot9}$ 1·09635, n_α^{24} 1·47354, n_D^{24} 1·47595, n_β^{24} 1·48708; the dimethyl ester $d_4^{25\cdot1}$ 1·14245, $n_\alpha^{25\cdot1}$ 1·48086, $n_D^{25\cdot1}$ 1·48347, $n_\beta^{25\cdot1}$ 1·49440. To obtain any considerable yield of reduction products from cyanocamphoric and homocamphoric esters, the reaction should be carried out at a temperature approaching 150°. This is also the case with the esters of carboxycamphoracetic acid, but only the ketonic group and the α-carbalkoxy-group are completely hydrogenated, the final product being the glycol. H. J. E.

Derivatives of Camphoronic Acid. W. F. GOEBEL and W. A. NOYES (*J. Amer. Chem. Soc.*, 1923, **45**, 3064—3070).—The investigation was undertaken in order to establish the structure of the various derivatives of camphoronic acid. The attempts to prepare either a dibasic amide or an anhydro-amide which would react with sodium hypobromite failed. Isomeric imide-amides were, however, obtained from the corresponding imides and have been found to react with sodium hypobromite. β-Anhydrocamphoronyl chloride reacts with ammonia to give transparent crystals of an *imide*, $C_9H_{13}O_4N$, m. p. 234·5—235°, $[\alpha]_D^{20}$ −5·40°. A *bromo-imide*, m. p. 220°, is similarly obtained from α-anhydrobromocamphoronyl chloride. *α-Camphoronamide-imide* is obtained by the action of phosphorus pentachloride and then anhydrous ammonia on α-camphoronimide. It forms transparent crystals, m. p. 235—236°, $[\alpha]_{5416}^{28}$ +11·87°. The *acid chloride* of β-camphoronimide is obtained from the imide and phosphorus pentachloride. It is a crystalline solid, m. p. 175·5—176·5° $[\alpha]_{5416}^{26}$ −18·32°. β-*Camphoronimide-amide* obtained by the action of ammonia on the β-imide chloride, is a crystalline solid, m. p. 205°, $[\alpha]_{5416}^{28}$ −13·73°. It reacts readily with sodium hypobromite. Potassium hydroxide fails to open the ring of either α- or β-camphoronimide, partial hydrolysis to the parent acid being the only reaction involved. F. G. P.

Oxidations with Ozone. I. The Preparation of Vanillin. E. BRINER, R. PATRY, and E. DE LUSERNA (*Helv. Chim. Acta*, 1924, **7**, 62—74).—The possibility of utilising ozone for technical oxidations is discussed, and experiments on the oxidation of *iso*eugenol to vanillin are recorded. The oxidations were carried out by conducting a current of ozonised air at varying concentrations of ozone (5% to 19%) into a solution of *iso*eugenol in carbon tetrachloride, at temperatures from −15° to +50°. The highest oxidation efficiency obtained, in terms of ozone consumed, was 20%, at the lowest temperature. At higher temperatures, the efficiency falls off rapidly and the quantity of resinous by-product formed increases. [Cf. *B.*, Apr.] E. H. R.

Phthalaldehyde. II. L. SEEKLES (*Rec. trav. chim.*, 1924, **43**, 93—102; cf. A., 1923, i, 931).—Attempts were made unsuccessfully to utilise the blue colour obtained by the reaction between phthalaldehyde, ammonia, and acetic acid for the determination of small quantities of ammonia. The reaction product appears to contain at least three different coloured substances, and the tint produced varies with the proportions of the reactants.

The dioxime of phthalaldehyde has not hitherto been prepared. It is now obtained in small yield by the action of hydroxylamine on phthalaldehyde in cold alcohol. *Phthalaldioxime* forms light yellow crystals containing $2H_2O$, m. p. 105° (indistinct), decomposing at 150°. The *di*-p-*nitrophenylhydrazone* of phthalaldehyde forms an orange precipitate (α-form), m. p. 244—245° (decomp.). By treatment with gaseous hydrogen chloride in chloroform solution it is converted into a red *isomeride* (β-form), decomposing violently at

208°. Attempts to prepare *iso*quinoline by the interaction of methylamine and phthalaldehyde were not successful. E. H. R.

Amino- and Oximo-derivatives of Thymoquinone. R. M. Hixon (*J. Amer. Chem. Soc.*, 1923, **45**, 2333—2341).—It is pointed out that quinones may be expected to add ammonia (or an amine), (*a*) at the carbonyl group, by analogy with the formation of aldehyde-ammonia, or (*b*) at the ethylenic bond, as do certain unsaturated aliphatic acids, and that actually both reactions probably occur with the quinones. The intermediate additive compound, derived from an amine and a quinone, is structurally analogous to an ammonium salt; this undergoes rearrangement, the amine becoming attached in either of the two ways mentioned. Such an intermediate complex, if formed from a tertiary amine, would be incapable of rearrangement. Actually Jackson and Clarke (A., 1905, i, 908) have reported that dimethylaniline yields coloured additive products with quinones. This is now qualitatively confirmed, since an additive compound appears to be formed when thymoquinone is dissolved in dimethylaniline (2 mols.). This is apparently stable when air and solvents are excluded, but otherwise a purple tar is produced, which, on hydrolysis by means of 50% sulphuric acid, gives both mono- and di-hydroxythymoquinone. This indicates to some extent that tertiary amines may react with quinones just as do primary and secondary amines.

Directions are given for the purification of nitrosothymol and of nitrosocarvacrol. Their benzoates are, in effect, hydrolysed when treated in dry heptane solution with dry methylamine gas. The reaction, which cannot be an ordinary hydrolysis, is explained by assuming the formation of an intermediate compound, structurally similar to aldehyde-ammonia, which undergoes rearrangement to give the nitroso-derivative and *N*-methylbenzamide. These benzoates form unstable *additive* compounds with concentrated nitric acid, having the formulæ and m. p., respectively, $C_{17}H_{17}O_2N,3HNO_3$, 53°, and $C_{17}H_{17}O_2N,2HNO_3$, 65°. Thymoquinone dioxime may be prepared more conveniently by the action of hydroxylamine hydrochloride on nitrosocarvacrol, yield 70%, than by using nitrosothymol, yield 6—10%. It forms a *dibenzoate*, colourless needles, m. p. 199—200° (becomes discoloured at 170°). W. S. N.

The Addition of Mercuric Salts to αβ-Unsaturated Ketones. E. B. Middleton (*J. Amer. Chem. Soc.*, 1923, **45**, 2763—2769).—αβ-Unsaturated ketones such as benzylideneacetophenone (phenyl styryl ketone) react with but one molecule of mercuric acetate, whilst dibenzylideneacetone (distyryl ketone) containing two double linkages reacts with 2 mols. of mercuric acetate. The products obtained in alcoholic solution show that the groups ·OR and $HgOCOCH_3$ have been added. The reactions of the additive compounds show that the mercury compounds of phenyl styryl ketone have the structure Ph·CH(OR)·CH(HgX)·COPh, whilst the derivatives of distyryl ketone are

Ph·CH(OR)·CH(HgX)·CO·CH(HgX)CH(OR)·Ph.

Substitution in the nuclei does not affect the reaction of the unsaturated ketones with mercuric acetate. Ketones of the *cyclo*propane series do not yield additive compounds. A comparison is made between the mercuric acetate additive compounds and the compounds obtained by Vorländer and Eichwald (A., 1923, i, 684), using the mercury halides. *α-Acetoxymercuri-β-methoxy-β-phenylpropiophenone*, $C_{18}H_{18}O_4Hg$, obtained by the action of mercuric acetate on phenyl styryl ketone in methyl alcohol, has m. p. 115°. The corresponding *ethoxy*-derivative has m. p. 134°. *α-Bromomercuri-β-methoxy-β-phenylpropiophenone*, $C_{16}H_{15}O_2BrHg$, m. p. 141°, is prepared by the action of potassium bromide on the acetoxy-compound. The *ethoxy*-compound has m. p. 138°. *α-Bromo-β-methoxy-β-phenylpropiophenone,* m. p. 76°, is obtained by adding bromine to the acetoxymercuric–methoxy-derivative of phenyl styryl ketone. The *ethoxy*-compound has m. p. 60—61° and the corresponding *iodo*-compounds 96° and 75—76°. Sodium methoxide converts α-bromo-β-methoxy-β-phenylpropiophenone into an oil, b. p. 200—205°/6 mm., addition of mercuric acetate to the oil yielding *diacetoxymercuridibenzoylmethane*, $C_{19}H_{16}O_6Hg_2$, m. p. 237°. The bromomethoxyphenylpropiophenone reacts with ethyl magnesium bromide to yield β-phenylvalerophenone, $C_{17}H_{18}O$, m. p. 63°. Distyryl ketone reacts with mercuric acetate to form the dimercurated compound containing two methoxy- and two mercuri-groups, m. p. 183°. *α-Acetoxymercuri-β-methoxy-β-phenyl-p-chloropropiophenone,* m. p. 124°, is obtained from mercuric acetate and *p*-chlorophenyl styryl ketone in methyl alcohol solution. F. G. P.

Preparation of 2 : 4 : 2′ : 4′-Tetrahydroxybenzophenone. J. B. Shoesmith and J. Haldane (*J. Chem. Soc.*, 1924, **125**, 113—115).—2 : 4-Diacetoxybenzonitrile is condensed with resorcinol by means of zinc chloride and dry hydrogen chloride, the resulting imine hydrochloride, $(AcO)_2C_6H_3\cdot C(:NH,HCl)\cdot C_6H_3(OH)_2$, being readily hydrolysed to the required benzophenone in acid solution. A certain amount of resacetophenone and of β-resorcylamide may be recovered from the reaction mixture. 2 : 4-*Diacetoxy-2′ : 4′-dihydroxybenzophenoneimine hydrochloride* gives crystals decomposing at 195°. F. G. P.

The Benzil Rearrangement. V. Cannizzaro's Reaction. A. Lachman (*J. Amer. Chem. Soc.*, 1923, **45**, 2356—2363).—In the Cannizzaro reaction, benzyl benzoate is formed from benzaldehyde, even in the presence of water, provided an excess of alkali is avoided and any considerable rise in temperature is prevented. It is suggested that dihydroxydibenzyl ether, $[CHPh(OH)]_2O$, is formed as an intermediate stage, and by a glycol rearrangement is converted into the benzoate. In the course of the investigation it was shown that by heating benzyl alcohol in a sealed tube at 210—215°, dibenzyl ether is obtained, and that bromine reacts with dibenzyl ether to produce benzyl bromide and benzoyl bromide. F. G. P.

The Isomerism of the Oximes. XV. The Alleged Fourth Benzildioxime. O. L. Brady and F. P. Dunn (*J. Chem. Soc.*, 1924, **125**, 291—296).—The work of Atack and Whinyates (T., 1921, **119**, 1184) has been repeated, but the authors have been unable to confirm the results, no evidence of the existence of the fourth dioxime being obtained. The purely structural theory of the isomerism of the oximes suggested by Atack is criticised and the principal objections to it are stated, particularly the existence of two *O*-ethers. F. G. P.

Dioximes. XVI. G. PONZIO and V. BERNARDI (*Gazzetta*, 1923, **53**, 813—817; cf. this vol., i, 54, 56).—The formation of the two benzildioximes from the two forms of phenylglyoxime by the action of phenyldiazonium chloride (A., 1923, i, 856) proves to be a reaction of general application constituting a new method of synthesising symmetrical and unsymmetrical, disubstituted glyoximes. Not only a glyoxime of the type $NOH{:}CAr{\cdot}CH{:}NOH$, in which Ar is an aryl radical, but also methylglyoxime, reacts with many aryldiazonium chlorides with liberation of nitrogen and formation of the glyoximes, $NOH{:}CR{\cdot}CR_1{:}NOH$. This reaction, which gives a yield of about 45%, is not so simple as is represented by the scheme,

$$NOH{:}CR{\cdot}CH{:}NOH+Ar{\cdot}N_2{\cdot}OH-H_2O \longrightarrow NOH{:}CR{\cdot}C(NOH){\cdot}N_2Ar-N_2 \longrightarrow NOH{:}CR{\cdot}CAr{:}NOH,$$

since there is entire lack of experimental evidence of the formation of an intermediate unstable compound with the N_2Ar group in direct union with a carbon atom. Participation in the reaction of the oximino-groups may, however, be excluded, since these pass with unaltered properties into the final products. Of special interest is the behaviour of methylglyoxime, which yields only the β-forms of glyoximes, $NOH{:}CMe{\cdot}CAr{:}NOH$; the conclusion that it is a β-modification is thus confirmed. Thus, β-phenylmethylglyoxime (A., 1922, i, 17) may be obtained by the action of phenyldiazonium chloride on methylglyoxime in 10% sodium hydroxide solution cooled with ice.

β-o-*Tolylmethylglyoxime*, $NOH{:}CMe{\cdot}C(NOH){\cdot}C_6H_4Me$, prepared from methylglyoxime and *o*-tolyldiazonium chloride, crystallises in white needles, m. p. 236° (slight decomp., and sublimation); its *nickel* salt, $(C_{10}H_{11}O_2N_2)_2Ni$, forms red prisms, m. p. 222°, and its *dibenzoyl* derivative, $C_{24}H_{20}O_4N_2$, prisms, m. p. 144°.

β-*p*-Tolylmethylglyoxime crystallises in white laminæ, m. p. 234—235°; Borsche (A., 1907, i, 326) gave m. p. above 230° (decomp.). Its *nickel* salt, $(C_{10}H_{11}O_2N_2)_2Ni$, forms blood-red prisms, m. p. 250—251° (decomp.), with previous browning, and its *dibenzoyl* compound, white needles, m. p. 148·5—149·5°.

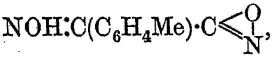
β-*p*-Anisylmethylglyoxime, prepared from *p*-methoxyphenyldiazonium chloride and methylglyoxime, forms white prisms, m. p. 213° (slight decomp.). Boeris (A., 1894, i, 72) gave m. p. 206°, and Tschugaev (A., 1908, i, 554), m. p. 207°; cf. also Wieland (A., 1903, i, 837). Its nickel salt, $C_{20}H_{22}O_6N_4Ni$, crystallises in scarlet needles, m. p. 224° (cf. Tschugaev, *loc. cit.*), and its *dibenzoyl* derivative in needles, m. p. 148·5°.

β-*Phenyl*-p-*tolylglyoxime*, $NOH{:}CPh{\cdot}C(NOH){\cdot}C_6H_4Me$, prepared by the interaction either of *p*-tolyldiazonium chloride and β-phenylglyoxime, or of phenyldiazonium chloride and β-*p*-tolylglyoxime, crystallises in lustrous laminæ, m. p. 223—224° (partial sublimation). Its *nickel* salt, $(C_{15}H_{13}O_2N_2)_2Ni$, forms microscopic, brick-red needles, m. p. 295—297° (decomp.), and its *dibenzoyl* derivative, laminæ, m. p. 184° (slight decomp.).

β-*Phenyl*-p-*anisylglyoxime*, $C_{15}H_{14}O_3N_2$, prepared similarly, crystallises in white laminæ, m. p. 223° (slight decomp.). Its *nickel* salt forms a microcrystalline, blood-red powder, m. p. 264° (decomp.), and its *dibenzoyl* derivative, laminæ, m. p. 162°.

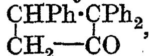
T. H. P.

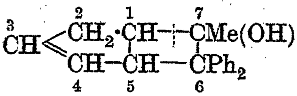
Dioximes. XVIII. L. Avogadro (*Gazzetta*, 1923, **53**, 824—828).—The dehydrogenating action of nitrogen tetroxide on the α-modifications of arylglyoximes proceeds similarly to that of the same reagent on α-phenylglyoxime (A., 1923, i, 1019, 1137). Thus, α-*p*-tolylglyoxime yields a compound which must be regarded as the oxide of *p*-toluoyl cyanide oxime since (1) with acetic anhydride it yields a monoacetyl derivative, (2) it is reduced by means of zinc and acetic acid, giving *p*-toluoyl cyanide oxime, (3) when heated with xylene it undergoes isomerisation to 5-hydroxy-3-*p*-tolyl-1 : 2 : 4-oxadiazole, (4) it unites with a molecule of ammonia to form amino-α-*p*-tolylglyoxime, and (5) it reacts with magnesium methyl iodide to form *p*-tolylmethylglyoxime.

The *oxide* of p-*toluoyl cyanide oxime*,  $NOH{:}C(C_6H_4Me){\cdot}C{<}\begin{smallmatrix}O\\|\\N\end{smallmatrix}$, or $NOH{:}C(C_6H_4Me){\cdot}C{:}N{:}O$, crystallises in silky, white needles, m. p. 108° with previous softening, and is highly stable towards acids, but is readily decomposed by bases or even by boiling water, giving *p*-toluonitrile and substances having the odour of carbylamine. Its *acetyl* derivative forms white prisms, m. p. 157—158°.

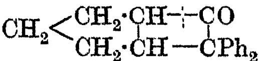
Amino-α-p-*tolylglyoxime*, $C_6H_4Me{\cdot}C({:}NOH){\cdot}C({:}NOH){\cdot}NH_2$, crystallises in white laminæ, m. p. 173—174°, and, when treated in aqueous alcoholic solution with nickel acetate, gives a greyish-green precipitate soluble in dilute acetic acid. When boiled with dilute acetic acid it slowly undergoes isomerisation into amino-β-*p*-tolylglyoxime, which has not been investigated further. T. H. P.

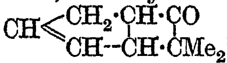
Ketens. XLVII. The Constitution of Dimeric Ketens, a Contribution to the Valency Problem of Organic Chemistry. H. Staudinger (*Helv. Chim. Acta*, 1924, 7, 3—8).—A reply to Schroeter (A., 1920, i, 852), who criticises the author's conception of the dimeric ketens as *cyclo*butan-1 : 3-diones or 1 : 3-*cyclo*butenolones, and considers them to be molecular compounds. The conception of dimeric aldoketens as 1 : 3-*cyclo*butenolone derivatives is supported by their physical properties and absorption spectra. Schroeter considers the more stable dimeric ketens to be true *cyclo*butandiones, the less stable to be molecular compounds, but it is pointed out that *cyclo*butane derivatives differ much in their stability to heat; substitution, including the keto-group, weakens the ring, and heavily substituted compounds such as ethyl diethyl*cyclo*butandionedicarboxylate are especially labile. The author's view is also supported by preparation of *cyclo*butane derivatives by the combination of diphenylketen with ethylenic compounds (A., 1920, i, 556, and following abstract). E. H. R.

Ketens. XLVIII. *cyclo*Butane Derivatives from Diphenylketen and Ethylenic Compounds. H. STAUDINGER and A. RHEINER (*Helv. Chim. Acta,* 1924, 7, 8—18).—The compound formed by diphenylketen with styrene is now found to be 1 : 1 : 4-*triphenyl*cyclo*butan-2-one*,  $\begin{array}{l}CHPh\cdot CPh_2\\ CH_2—CO\end{array}$, instead of the 1 : 1 : 3-compound as previously stated (Staudinger and Suter, A., 1920, i, 556). It follows that the acid obtained by treating it with sodium hydroxide in alcoholic solution is αα*β-triphenyl*-n-*butyric acid* instead of the ααγ-compound. Evidence for the constitution of the triphenyl*cyclo*butanone was obtained through the action of methyl magnesium iodide, by means of which the tertiary alcohol, 1-*methyl*-2 : 2 : 3-*triphenyl*cyclo*butan*-1-*ol* was obtained, colourless crystals, m. p. 132°; the yield was 87% of the theoretical. When rapidly distilled at the ordinary pressure, the tertiary alcohol decomposes to the extent of 80% into *as*-diphenylacetone and styrene and 20% into acetone and triphenylethylene. These products establish its constitution. When distillation is carried out in a high vacuum, decomposition does not take place, but an *isomeride* is formed, m. p. 137°; in all probability the ring has opened with formation of a triphenyl-*n*-propyl methyl ketone. By the action of phenyl magnesium bromide on the triphenyl*cyclo*butanone there is obtained, not the expected tertiary alcohol, but *benzylidenediphenylacetone*, $CHPh_2\cdot CO\cdot CH:CHPh$ [*benzhydryl styryl ketone*], m. p. 112°, b. p. 250°/18 mm. The same compound was synthesised from diphenylacetone and benzaldehyde (cf. Rack, A., 1923, i, 681).

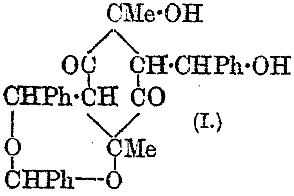


$\overset{3}{CH}<\begin{array}{l}\overset{2}{CH_2}\cdot\overset{1}{CH}-\vdots-\overset{7}{C}Me(OH)\\ \underset{4}{CH}-\underset{5}{CH}—\underset{6}{C}Ph_2\end{array}$

As previously described (*loc. cit.*), diphenylketen combines with *cyclo*pentadiene to form a compound, which can be reduced to a saturated compound, for which the formula  $CH_2<\begin{array}{l}CH_2\cdot CH-\vdots-CO\\ CH_2\cdot CH—CPh_2\end{array}$, is now proposed. When this is submitted to prolonged boiling with sodium hydroxide, hydrolysis takes place at the dotted line with formation of *diphenyl*cyclo*pentylacetic acid*, m. p. 85°; *anilide*, m. p. 139°. The compound of diphenylketen with *cyclo*pentadiene reacts with methyl magnesium iodide to give the tertiary alcohol having the annexed formula, designated 6 : 6-*diphenyl*-7-*methyl*-0 : 2 : 3-bicyclo-3 : 4(?)-*hepten*-7-*ol*, m. p. 130°. When boiled with alcoholic potassium hydroxide the heptane ring opens, probably at the dotted line, forming a *ketone*; its semicarbazone has m. p. 115°. By treatment with hydrogen and platinum black, the above heptenol is reduced to the corresponding *heptanol*, m. p. 99°. By the action of phenyl magnesium iodide on the diphenylketen–*cyclo*pentadiene compound, a *substance* was obtained, m. p. 214°, having the same empirical composition as the original compound. It may be a dimeride. Diphenylketen and di*cyclo*pentadiene form a *compound*, m. p. 95°. E. H. R.

Ketens. XLIX. *cyclo*Butane Derivatives from Dimethylketen and Ethylenic Compounds. H. STAUDINGER and P. J. MEYER (*Helv. Chim. Acta*, 1924, **7**, 19—22).—Dimethylketen combines less readily with ethylenic compounds than diphenylketen, but the compounds when formed are more stable than those from diphenylketen. The four-membered ring is relatively stable and the ketonic group has normal properties. Dimethylketen does not combine with styrene, but with vinyl ethyl ether it forms 3(or 4)-*ethoxy*-1 : 1-*dimethyl*cyclo*butan*-2-*one*, a colourless oil, b. p. 166—169°; the *phenylhydrazone* forms white needles, m. p. 70°, and quickly decomposes in the air. With *cyclo*pentadiene, dimethylketen forms a *compound* probably having the formula 
$CH{<}^{CH_2\cdot CH\cdot CO}_{CH{-}{-}CH\cdot CMe_2}$, but the position of the double bond is uncertain; it is an oil with a camphor-like odour, b. p. 175—178°; when superheated it decomposes into dimethylketen and *cyclo*pentadiene. Its *semicarbazone* has m. p. 215°. When reduced with hydrogen and platinum black it gives the saturated compound, 6 : 6-*dimethyl*-0 : 2 : 3-bicyclo*heptan*-7-*one*, also having the odour of camphor, b. p. 176—178°; it gives dimethylketen when superheated. Its *semicarbazone* has m. p. 224°. E. H. R.

Reaction Products from Aldehydes and 1 : 2-Diketones. O. DIELS [with R. W. POINDEXTER, K. ILBERG, and W. GÄDKE] (*Annalen*, 1923, **434**, 1—20).—When a mixture of benzaldehyde and diacetyl is treated at − 10° with 25% methyl-alcoholic potassium hydroxide solution, the diketone first polymerises to its dimeride, 1 : 4-dihydroxy-1 : 4-dimethyl*cyclo*hexan-3 : 6-dione (Diels, Blanchard, and v. d. Heyden, A., 1914, i, 1052); this then undergoes condensation with the aldehyde (3 mols.), 1 mol. of water being eliminated, with the formation of the same *compound* (I), slender, white needles, m. p. 198° (decomp.), which is obtained if the dimeride itself is used. The structure of this substance is evident from the following reactions. Although, probably owing to steric hindrance, the ketone groups are not reactive, the hydroxyl group next to the phenyl radical can be esterified. The *benzoate* forms thick, transparent prisms, m. p. 192°; the *acetate*, four-sided tablets or prisms, has m. p. 197—198°. But if, in preparing the acetate, the action of acetic anhydride is continued, water is eliminated, with the production of the unsaturated *acetate*, $-OC\cdot CMe{:}C(CHPh\cdot OAc)\cdot CO-$, m. p. 237°. This compound reacts immediately with potassium permanganate in glacial acetic acid solution, or with bromine in cold chloroform solution; the subsequent spontaneous elimination of hydrogen bromide from the dibromide produced in the latter reaction gives two *bromo*-derivatives, $C_{31}H_{27}O_6Br$, (*a*) colourless needles, or



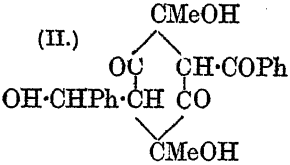
(I.)

small, elongated plates, m. p. 193°, (*b*) small, transparent prisms, m. p. 210°. The action of phenylhydrazine in methyl-alcoholic glacial acetic acid solution at 65° on the unsaturated acetate gives the corresponding unsaturated *alcohol*, m. p. 198—203°, $+x\mathrm{EtOH}$, long prisms, which is readily converted into the compound (I) by boiling with hydrochloric, acetic, or propionic acid, and gives the saturated *methyl* ether, $-\mathrm{OC{\cdot}CMe(OMe){\cdot}CH(CHPh{\cdot}OH){\cdot}CO}-$ (felted needles, m. p. 240°, after decomposing at 218°), when boiled with methyl alcohol containing a trace of hydrochloric acid. Similarly, the action of acids on the unsaturated acetate gives the saturated acetate, which, like the analogous benzoate, is readily hydrolysed to the compound (I) by means of boiling alcoholic potassium hydroxide solution. By the action of a boiling mixture of glacial acetic acid and concentrated nitric acid on the compound (I), the secondary alcohol group is oxidised to a ketone group,

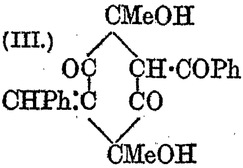
$$-\mathrm{CO{\cdot}CMe(OH){\cdot}CH(COPh){\cdot}CO}-,$$

with the formation of a *compound*, m. p. 203—204° (decomp.), which crystallises from acetonitrile with 1MeCN, in rhombic crystals, readily soluble in alkali. In 25% methyl-alcoholic potassium hydroxide solution, benzaldehyde is rapidly eliminated, with the production of the *compound* (II), thin, felted needles, m. p. 151—153° after sintering at about 146°. The latter is soluble in aqueous alkali, but soon resinifies, more rapidly on warming, with the elimination of benzaldehyde. It is converted by the action of methyl alcohol containing hydrogen chloride into its *methyl* ether, compact, snow-white crystals, m. p. 169—171° (slight decomp.); methyl hydrazinecarboxylate gives a *salt*, felted needles, m. p. 130—132° (decomp.), in the formation of which, presumably, the benzoyl group has taken part in its enolic form. The ketonic groups are not reactive. The compound (II) forms an additive *compound* with cold formic acid, but the boiling, anhydrous reagent causes the elimination of water, to give 2-*benzoyl*-1 : 4-*dihydroxy*-5-*benzylidene*-1 : 4-*dimethyl*cyclo*hexan*-3 : 6-*dione* (III), a bright sulphur-yellow compound, m. p. 238—243°, one of the ketone groups of which is reactive; the *oxime*, m. p. 221—222°, *semicarbazone*, long, colourless needles, decomp. about 235°, m. p. 245—248°, and the *carbomethoxyhydrazone*, long, colourless prisms, decomp. 220°, m. p. 240—243°, are described. The compound (III) is decomposed at 250—270° into benzoyldiacetyl and benzylidenediacetyl.

(II.)



(III.)



Compounds are also prepared by condensing diacetyl with furfurol and anisaldehyde. The first forms thick, colourless needles, m. p. 203° (decomp.) after sintering at 180°; the second forms small needles, and has m. p. 203—205° (decomp.). With concentrated sulphuric acid they give, respectively, a dark reddish-purple coloration, which changes to brown, and an intense carmine coloration, which persists during twenty-four hours. W. S. N.

Trihydroxymethylanthraquinones. I. G. D. GRAVES and R. ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 2439—2455).—3 : 6-Dimethoxyphthalic anhydride is prepared by the action of boiling 98% sulphuric acid on the dimethyl ether of 2 : 3-dicyanoquinol, which is obtained by the action of potassium hydroxide solution and methyl sulphate on 2 : 3-dicyanoquinol.

The action of an excess of *p*-cresol on 3 : 6-dimethoxyphthalic anhydride in the presence of aluminium chloride at 70° gives 3 : 6-*dimethoxy*-2-(2′-*hydroxy*-5′-*methylbenzoyl*)*benzoic acid*, white plates, m. p. 218° (corr.), together with 12 : 15-*dimethoxy*-2 : 7-*dimethylfluoran*, white crystals, m. p. 290° (corr.). When the benzoic acid derivative is boiled with potassium hydroxide solution and methyl sulphate, the product is 3 : 6-*dimethoxy*-2-(2′-*methoxy*-5′-*methylbenzoyl*)*benzoic acid*, white needles, or colourless, truncated prisms, m. p. 203—204° (corr.), which is identical with the product from 3 : 6-dimethoxyphthalic anhydride and *p*-cresyl methyl ether (cf. following abstract). When the substituted benzoic acid and concentrated sulphuric acid are heated at 100° with a small quantity of boric acid, the colour changes from green to bluish-red, owing to the formation of 1-*hydroxy*-5 : 8-*dimethoxy*-4-*methylanthraquinone*, red needles, m. p. 224° (corr.). The latter is demethylated by boiling with glacial acetic acid and hydrobromic acid (constant-boiling), giving 1 : 5 : 8-*trihydroxy*-4-*methylanthraquinone*. When 3 : 6-dimethoxyphthalic anhydride is heated at 75° with an excess of *o*-cresol in the presence of aluminium chloride, the products are 3 : 6-*dimethoxy*-2-(2′-*hydroxy*-3′-*methylbenzoyl*)*benzoic acid*, white needles, m. p. 194° (corr.), and o-*cresol*-3 : 6-*dimethoxyphthalein*, white needles, m. p. 258° (corr.). The latter is an indicator, changing from colourless to red at p_H 9·1. The methylation of the benzoic acid gives 3 : 6-*dimethoxy*-2-(2′-*methoxy*-3′-*methylbenzoyl*)-*benzoic acid*, white needles, m. p. 178° (corr.), which is not identical with the acid formed by condensing 3 : 6-dimethoxyphthalic anhydride with *o*-cresyl methyl ether; in the latter reaction, there is also formed the *dimethyl ether* of *o*-cresol-3 : 6-dimethoxyphthalein, white needles, m. p. 202° (corr.), which is likewise produced by the methylation of the phthalein. The action of sulphuric acid, containing boric acid, on the benzoic acid derivative, gives 1-*hydroxy*-5 : 8-*dimethoxy*-2-*methylanthraquinone*, red needles, m. p. 165° (corr.), which may be demethylated to give 1 : 5 : 8-*trihydroxy*-2-*methylanthraquinone*, red needles, which sublime at 250—260°. When *o*-cresol-3 : 6-dimethoxyphthalein and 3 : 6-dimethoxyphthalic anhydride are heated at 125° with concentrated sulphuric acid, the product is 2 : 5 : 8-*trihydroxy*-1-*methylanthraquinone*, dark red needles, m. p. 270° (corr.), which is identical with the product obtained by condensing 3 : 6-dimethoxyphthalic anhydride with *o*-cresyl methyl ether, dehydrating the benzoylbenzoic acid thus obtained, and hydrolysing the resulting anthraquinone. The interaction of 3 : 6-dimethoxyphthalic anhydride and *m*-cresol at

75° in the presence of aluminium chloride gives 3 : 6-*dimethoxy-2-(2′-hydroxy-4′-methylbenzoyl)benzoic acid*, white needles, m. p. 233° (corr.), and 3-*hydroxy-6-methoxy-2-(2′-hydroxy-4′-methylbenzoyl)benzoic acid*, white needles, m. p. 189° (corr.). A third substance formed in the above reaction is m-*cresol-3 : 6-dimethoxyphthalein*, white needles, m. p. 271° (corr.), a solution of which changes from colourless to red at p_H 9·8. The conversion of 3 : 6-dimethoxy-2-(2′-hydroxy-4′-methylbenzoyl)benzoic acid into 1-*hydroxy-5 : 8-dimethoxy-3-methylanthraquinone*, red needles, m. p. 172° (corr.), can only be accomplished by the use of fuming sulphuric acid at 100° in the presence of boric acid. The demethylation of this dimethoxyanthraquinone by means of glacial acetic acid and hydrobromic acid gives 1 : 5 : 8-*trihydroxy-3-methylanthraquinone*, red needles, m. p. 227° (corr.).

The condensation of 3 : 5-dimethoxyphthalic anhydride with *m*-cresol by heating with aluminium chloride at 70° gives 3 : 5-*dimethoxy-2-(2′-hydroxy-4′-methylbenzoyl)benzoic acid*, white needles, m. p. 233° (corr.), and m-*cresol-3 : 5-dimethoxyphthalein*, which cannot be purified. The former gives, on methylation, 3 : 5-*dimethoxy-2-(2′-methoxy-4′-methylbenzoyl)benzoic acid*, white needles, m. p. 219° (corr.), whereas the condensation of 3 : 5-dimethoxyphthalic anhydride with *m*-cresyl methyl ether gives 3 : 5-*dimethoxy-2-(4′-methoxy-2′-methylbenzoyl)benzoic acid*, m. p. 233° (corr.). The action of fuming sulphuric acid and boric acid at 100° on 3 : 5-dimethoxy-2-(2′-hydroxy-4′-methylbenzoyl)benzoic acid leads to sulphonation, a poor yield of the expected *anthraquinone*, yellow needles, m. p. about 185°, being obtained. This substance gives a red solution in alkali, which reacts with methyl sulphate at 100° to give a *trimethoxy* compound, yellow needles, m. p. about 175—180°, which gives a red solution in concentrated sulphuric acid, and should be the trimethyl ether of emodin, if the latter has the structure suggested (*Arch. Pharm.*, 1912, **250**, 301). The action of concentrated nitric acid in glacial acetic acid solution at 50—60° on 3 : 5-dimethoxy-2-(2′-hydroxy-4′-methylbenzoyl)benzoic acid gives the 5′-*nitro*-derivative, pale yellow needles, m. p. 241° (corr.), but the product of the condensation of 3 : 5-dimethoxyphthalic anhydride and *o*-nitro-*m*-cresol is 3 : 5-*dimethoxy-2-(4′-hydroxy-5′-nitro-2′-methylbenzoyl)benzoic acid*, white needles, m. p. 181° (corr.).

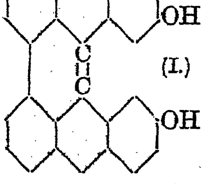
3 : 5-Dimethoxyphthalic acid is obtained by the action of cold, alkaline, potassium permanganate solution on 3 : 5-dimethoxyphthalide, which is prepared by heating its carboxylic acid. The latter is made by the action of warm sodium hydroxide solution on 3 : 5-dimethoxytrichloromethylphthalide, which is formed when a mixture of chloral hydrate and ethyl 3 : 5-dimethoxybenzoate is treated with somewhat concentrated sulphuric acid. W. S. N.

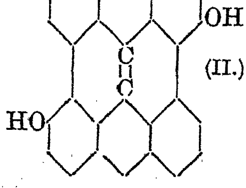
Trihydroxymethylanthraquinones. II. J. H. GARDNER and R. ADAMS (*J. Amer. Chem. Soc.*, 1923, **45**, 2455—2462; cf. preceding abstract).—The action of an excess of *p*-cresyl methyl ether on 3 : 6-dimethoxyphthalic anhydride at 70° in the presence of aluminium chloride gives 3 : 6-dimethoxy-2-(2′-methoxy-5′-methylbenzoyl)benzoic acid, together with the *dimethyl ether* of *p*-cresol-3 : 6-dimethoxyphthalein, colourless needles, m. p. 187·5° (corr.). When the trimethoxybenzoic acid is rapidly heated with concentrated sulphuric acid at 150°, and then cooled, the products are 1-hydroxy-5 : 8-dimethoxy-4-methylanthraquinone and 1 : 5 : 8-*trihydroxy-4-methylanthraquinone*, slender, red needles, m. p. 276—278° (corr.) (with sublimation); the latter is the sole product if the reaction mixture is kept at 145—155° for twenty minutes. When a mixture of 3 : 6-dimethoxyphthalic anhydride and an excess of *o*-cresyl methyl ether is treated at 65° with aluminium chloride, there are formed 3 : 6-*dimethoxy-2-(4′-methoxy-5′-methylbenzoyl)benzoic acid*, a white powder, m. p. 192° (corr.), and the *dimethyl ether* of *o*-cresol-3 : 6-dimethoxyphthalein, colourless needles, m. p. 202—203° (corr.). When the acid is rapidly heated with concentrated sulphuric acid at 150°, and immediately cooled, the chief product is 5 : 8-*dihydroxy-2-methoxy-1-methylanthraquinone*, dark red needles, m. p. 249—249·5° (corr.), which is accompanied by a small quantity of 2 : 5 : 8-trihydroxy-1-methylanthraquinone. The latter may more conveniently be prepared by heating a mixture of concentrated sulphuric acid, 3 : 6-dimethoxyphthalic anhydride, and *o*-cresol-3 : 6-dimethoxyphthalein, or its dimethyl ether, at 125°. The structure of the original benzoic acid is proved by distilling the trihydroxyanthraquinone with zinc dust, the resulting methylanthracene being then oxidised to 1-methylanthraquinone. 3-*Hydroxy-6-methoxy-2-(4′-methoxy-1′-methylbenzoyl)benzoic acid*, colourless prisms, m. p. 194—195° (corr.), and not the dimethoxy-acid, is obtained when 3 : 6-dimethoxyphthalic anhydride is treated with an excess of *m*-cresyl methyl ether and aluminium chloride at 75°; a phthalein is not produced. A pure derivative of anthraquinone has not been obtained by the dehydration of this acid.

W. S. N.

Reduction Products of the Hydroxyanthraquinones. IV.

J. W. E. Haller and A. G. Perkin (*J. Chem. Soc.*, 1924, **125**, 231—239).—Reduction of 2-hydroxyanthraquinone with glucose and alkali in the presence of sodium nitrate yields 2-hydroxybenzanthronecarboxylic acid, and two compounds which are now shown to be 3 : 6′-dihydroxyhelianthrone, $C_{28}H_{14}O_4$ (I), and 3 : 6′-dihydroxy-*meso*naphthadianthrone, $C_{28}H_{12}O_4$ (II). Better yields of (I) are obtained by the oxidation of dihydroxydianthrone with potassium ferricyanide. (II) may be obtained by exposing the diacetyl derivative of (I) (in benzene or acetic acid solution) to sunlight for some weeks, when an almost quantitative yield of the diacetoxynaphthadianthrone


(I.)

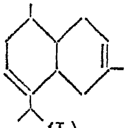

(II.)

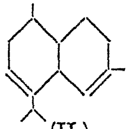
results. Oxidation of the acetyl compound of (I) with chromic acid yields *diacetoxy*-1 : 1′-*dianthraquinonyl*, $C_{28}H_{12}O_6Ac_2$, small plates, m. p. 277°. The corresponding *dihydroxy* compound crystallises in prisms or leaflets, m. p. >350°. The *dimethyl ether*, $C_{30}H_{18}O_6$, crystallises in yellow prisms, m. p. 343—344°. With iodine in pyridine solution, (I) yields 5-*iodo*-3 : 6′-*diacetoxyhelianthrone*, $C_{32}H_{17}O_6I$, yellow needles, m. p. 282°, and from this by hydrolysis the *dihydroxy* compound is obtained in the form of scarlet needles, m. p. >350°. 3 : 6′-*Dihydroxynaphthadianthrone*, $C_{28}H_{12}O_4$, is an orange-brown powder, m. p. >350°. Its *diacetyl* derivative crystallises in yellow needles. F. G. P.

Camphorylcarbamates and their Physiological Action. H. E. Fierz-David and W. Müller (*J. Chem. Soc.*, 1924, **125**, 26—27).—Camphorylcarbamates may be obtained in almost quantitative yield by the interaction of aminocamphor and alkyl chloroformates. Their pronounced poisonous action renders them unsuitable for practical application. iso*Amyl* and *allyl camphorylcarbamates* are viscous, oily liquids, b. p. 199°/11 mm., and 186°/10 mm., respectively, with $[\alpha]_D$ +34·2°, +34·3°. *Methyl camphorylcarbamate*, m. p. 110°, b. p. 169°/11 mm., $[\alpha]_D$ +39·4°. The *ethyl*, iso*propyl*, and iso*butyl* derivatives have, respectively, m. p. 88°, 73°, 83°; b. p. 178°/13 mm., 170°/10 mm., 184°/11 mm., with $[\alpha]_D$ +35·1°, 35·3°, and 33·9°. F. G. P.

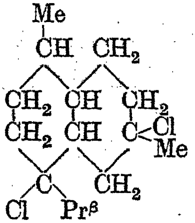
Piperitone. VII. The Constitution of Piperitone. J. Read, H. G. Smith, and R. S. Hughesdon (*J. Chem. Soc.*, 1924, **125**, 129—137).—Benzyl-*dl*-*iso*menthone, obtained by hydrogenation of benzylidene-*dl*-piperitone, is distinct from 2-benzyl-*dl*-*iso*menthone obtained, from *dl*-piperitone. It is concluded from this observation that piperitone is Δ^1-*p*-menthen-3-one, and benzylidenepiperitone is 6-benzylidene-Δ^1-*p*-menthen-3-one. 6-Benzyl-*dl*-*iso*menthone reacts with benzaldehyde to yield 2-benzylidene-6-benzyl-*dl*-*iso*menthone, and it also forms a semicarbazone, whilst 2-benzyl-*dl*-*iso*menthone is incapable of so reacting. 2-*Benzylidene*-dl-iso*menthone hydrochloride* forms colourless needles, m. p. 108—110°. 2-*Benzyl*-dl-iso*menthol*, $C_{10}H_{19}O{\cdot}CH_2Ph$, is a colourless, viscid liquid, b. p. 194—196°/20 mm. Its *phenylurethane* melts at 153—154°. 2-*Benzylidene*-dl-iso*menthone*, $C_{10}H_{16}O{:}CHPh$, is a colourless liquid, b. p. 193—195°/15 mm. The corresponding *benzyl* compound, $C_{10}H_{17}O{\cdot}CH_2Ph$, is a colourless, viscid liquid, b. p. 195—197°/20 mm., d_4^{20} 0·9957, n_D^{20} 1·5230, and $[R_L]_D$ 74·92. 6-*Benzyl*-dl-iso*menthone*, $C_{10}H_{17}O{\cdot}CH_2Ph$, is a colourless, viscid liquid, b. p. 202—203°/14 mm., d_4^{20} 0·9884, n_D^{20} 1·5176, and $[R_L]_D$ 74·84. Its *semicarbazone* crystallises in colourless prisms, m. p. 170—171°. 6-Benzyl-*dl*-*iso*menthone distils at 213—220°/20 mm., and has d_4^{20} 0·9905, n_D^{20} 1·5239, and $[R_L]_D$ 75·42. Its *semicarbazone* has m. p. 170—171°. 6-*Benzyl*-2-*benzylidene*-dl-iso*menthone* is a yellow, mobile oil, b. p. 218—225°/15 mm. Reduction of this yields 2 : 6-*dibenzyl*-dl-iso*menthol*, a pale yellow, viscid liquid, b. p. 282—287°/23 mm. 6-*Benzyl*-dl-iso*menthol*, $C_{10}H_{19}O{\cdot}CH_2Ph$, distils at 203—207°/16 mm. Its *phenylurethane* crystallises in needles and has m. p. 138—139°. A crystalline variety of the *iso*menthol, m. p. 66—68°, has also been obtained. F. G. P.

Higher Terpene Compounds. XVIII. The Constitution of Cadinene. L. Ruzicka and M. Stoll (*Helv. Chim. Acta*, 1924, 7, 84—94).—The carbon framework of cadinene has already been established by its dehydrogenation with sulphur to cadaline (Ruzicka and Meyer, A., 1921, i, 573). This result has now been confirmed by the catalytic dehydrogenation of cadinene with platinum black in a high vacuum at 300°. It remains therefore to determine the positions of the two double bonds. That one of these is probably adjacent to the *iso*propyl group has already been shown (Ruzicka and Seidel, A., 1922, i, 562). It is now shown, by a variety of arguments, that cadinene is probably to be represented by one or both of the two annexed formulæ.

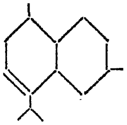

(I.)

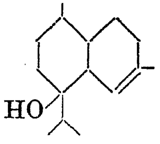

(II.)

The products obtained by the action of ozone on cadinene, followed by decomposition of the ozonide first formed, render it extremely improbable that both double bonds are contained in the same ring. Although great difficulty was experienced in obtaining any identifiable products from this reaction, an *ethyl dicarboxylate* was obtained, b. p. 190—200°/0·2 mm., having the composition $C_{19}H_{30}O_5$ or $C_{19}H_{32}O_6$, in which all the carbon atoms of cadinene are intact. The absence of conjugated double bonds in cadinene is shown by the failure of attempts at reduction with sodium and amyl alcohol. The oxidation of cadinene with manganese dioxide and sulphuric acid as described by Ruzicka, Schinz, and Meyer (this vol., i, 171) resulted in the formation of trimellitic acid and mellophanic acid as primary products, and benzenepentacarboxylic acid as a secondary product. Cadinene dihydrochloride can be definitely stated to have the annexed formula. E. H. R.

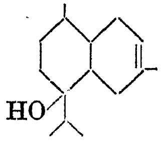


Higher Terpene Compounds. XIX. Cadinol from Galbanum Oil. L. Ruzicka and M. Stoll (*Helv. Chim. Acta*, 1924, 7, 94—105).—A sesquiterpene alcohol, cadinol, $C_{15}H_{26}O$, which by loss of a molecule of water gives cadinene, was discovered by Semmler and Jonas in galbanum resin (A., 1915, i, 573). Having elucidated the constitution of cadinene (preceding abstract), the authors now attempt to discover that of cadinol. The compound does not react at a high temperature with phthalic anhydride, and must therefore be a tertiary alcohol. To determine the position of the double bond and of the hydroxyl group, the action of ozone was studied on cadinol itself and on the dihydrocadinene obtained by hydrogenating cadinol and then removing water. An attempt to reduce cadinol to a dihydrocadinene by heating with zinc dust was unsuccessful; only cadinene was obtained, by dehydration of the cadinol. Reduction of cadinol to *dihydrocadinol* was effected with some difficulty by hydrogen and platinum black; it is a colourless oil, b. p. 150—153°/12 mm., $[\alpha]_D$ +23°, n_D^{16} 1·4948, d_4^{16} 0·9579. By boiling with 90% formic acid, dihydrocadinol is converted into *dihydrocadinene* (annexed formula), a colourless oil, b. p. 129—131°/12 mm., $[\alpha]_D$ +19·8°, n_D^{13} 1·4952, d_4^{13} 0·8999. By the action of ozone on this compound and decomposition of the ozonide there were obtained a keto-aldehyde and a keto-acid by the disruption of the hydrocarbon at the double bond; neither, however, was obtained in a pure condition. By ozonisation of cadinol itself there was obtained a neutral product, $C_{15}H_{24}O_2$, probably a *ketone–alcohol*, b. p. 180—184°/12 mm.; it contains one double bond. In addition a doubly unsaturated *ketone*, $C_{15}H_{22}O$, probably formed from the previous compound by loss of water, was obtained, b. p. 140—145°/12 mm. Oxidation of this ketone with manganese dioxide and sulphuric acid gave only mellophanic acid. The higher-boiling fractions of the neutral products from the ozonisation of cadinol gave, besides mellophanic acid, trimellitic acid. These observations can be explained on the assumption that cadinol consists of at least two forms, α and β, with probably a small proportion of a third form, γ, having the formulæ :

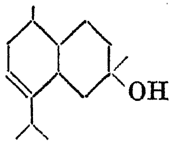




α-Cadinol.



β-Cadinol.



γ-Cadinol.

Structural formulæ are suggested for the products obtained by the ozonisation of cadinol, based on the above formulæ for cadinol. The cause of the formation of trimellitic acid by oxidation of higher fractions of these products is traced back to the small proportion of γ-cadinol probably present in the cadinol. E. H. R.

The Chlorohydrins of β-Pinene. G. G. HENDERSON and C. A. KERR (*J. Chem. Soc.*, 1924, **125**, 102—106).—β-Pinene, on treatment with a very dilute aqueous solution of hypochlorous acid, gives mainly a mixture of three isomeric crystalline *dichlorohydrins*, $C_{10}H_{18}O_2Cl_2$, of m. p. 135°, 166°, and 131°, respectively. They are isomeric but not identical with the corresponding compounds prepared from α-pinene. The dichlorohydrin of m. p. 135° is converted into a *monochlorohydrin*, $C_{10}H_{17}O_2Cl$, m. p. 128—129°, by the action of dilute potassium hydroxide solution; this is an isomeride of pinol glycol chlorohydrin. Further action of caustic alkali converts it into an oily liquid which is apparently somewhat similar to pinol oxide in properties. The dichlorohydrin, m. p. 166°, also yields an oily liquid on treatment with caustic alkali, but a solid monochlorohydrin could not be obtained in this case. The third dichlorohydrin, m. p. 131°, is unaffected by caustic alkali in the cold. F. G. P.

Some Oxidation Products of β-Pinene. G. G. HENDERSON and D. CHISHOLM (*J. Chem. Soc.*, 1924, **125**, 107—113).—β-Pinene unites with chromyl chloride to form a solid *compound*, $C_{10}H_{16}\cdot 2CrO_2Cl_2$, which on decomposition by water yields as chief product the ketone $C_9H_{14}O$, previously prepared in a similar fashion from α-pinene. A trace of an aldehyde and a small quantity of the inactive form of *trans*-pinol glycol were also obtained. Oxidation of β-pinene in glacial acetic acid solution by hydrogen peroxide gives a mixture of volatile and non-volatile products, the chief constituents of the volatile portion being borneol and a little fenchyl alcohol. The non-volatile portion could not be obtained sufficiently pure for identification. F. G. P.

Diacetyl Compound of Desmotropo-Artemisin. P. BERTOLO (*Gazzetta*, 1923, **53**, 867—869).—It is now found that desmotropo-artemisin forms a diacetyl derivative, so that, in the transformation of artemisin into desmotropo-artemisin, the fourth oxygen atom retains its alcoholic character (cf. A., 1923, i, 1108).

Diacetyldesmotropo-artemisin, $C_{19}H_{22}O_6$, crystallises in hard, lustrous, white needles, often grouped in radiating masses, m. p. 149—150°, $[\alpha]_D^{25}$ −50·75° (in alcohol). When hydrolysed by means of alcoholic potassium hydroxide, it yields, not artemisin, but a moderately stable, acid compound, m. p. above 200°, which is apparently identical with that obtained by hydrolysis of the acetyl derivative of artemisin (*loc. cit.*). T. H. P.

The Formation of Free Radicals by Reduction with Vanadous Chloride. J. B. CONANT and A. W. SLOAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2466—2472).—The addition of vanadous chloride solution to a solution of triphenylpyrylium chloride, or of its ferric chloride double salt, in the absence of air, causes the formation of a red precipitate, which is thought to be a *free radical.* With chloroform or benzene, it gives a red solution, the colour of which disappears when it is shaken with air. The substance is reoxidised to the pyrylium salt when it is treated in aqueous suspension with a solution of a ferric salt; if this process is conducted in the absence of oxygen, using freshly prepared material, a maximum of 1 mol. of ferric salt is required, but much less than this is needed if the compound, which is evidently unstable, has been kept for a few hours, even in an atmosphere of carbon dioxide.

The action of an excess of vanadous chloride on 9-phenylxanthylium chloride, in hydrochloric acid solution, in the absence of air, gives Gomberg and Cone's free radical, phenylxanthyl, which is identified by conversion into its peroxide.

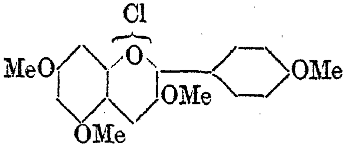
Triphenylcarbinol, in concentrated hydrochloric acid or concentrated sulphuric acid solution, is reduced by means of vanadous chloride in an atmosphere of carbon dioxide to triphenylmethyl, which is likewise identified by means of the peroxide.

The action of vanadous chloride on a very dilute solution of xanthylium chloride in concentrated hydrochloric acid gives a pink solid, which may be kept for a few hours in air at the ordinary temperature, but gradually changes to the colourless dixanthyl. Attempts to dry it in an atmosphere of nitrogen without loss of colour have been unsuccessful. When the bright pink solid is washed with water, drained, and dissolved in chloroform in an atmosphere of nitrogen, the solution is momentarily red; this colour disappears in the course of a few seconds. It is evident, from the last experiment, that polymerisation, and not oxidation, causes the change to dixanthyl. There is therefore strong evidence that the pink solid is the free radical, *xanthyl*.

The addition of vanadous chloride to an aqueous solution of benzylpyridinium chloride does not cause the formation of a precipitate, although the first portions of vanadous chloride undergo a change of colour; after making the solution alkaline, however, *N* : *N'*-dibenzyltetrahydrodipyridyl may be extracted from the solution by means of ether. W. S. N.

Chloro- and Amino-anthracoumarins. V. I. MINAEV (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 680—684).—A short abstract of this work has already appeared (A., 1922, i, 162); the preparation of the following additional compounds is now described: 8-*amino-anthracoumarin*, from *m*-aminocinnamic and *m*-hydroxybenzoic acid, silvery crystals resembling β-naphthol, softens at 285°, carbonises at about 300°; 8-*chloroanthracoumarin*, obtained in a similar way from *m*-chlorocinnamic acid, forms brown crystals, m. p. 241°; gives on sublimation golden-yellow needles, m. p. 329°; 9-*aminoanthracoumarin*, obtained by condensing *p*-aminocinnamic acid and *m*-hydroxybenzoic acid, and the corresponding *chloro*-compound, were also prepared, but their properties are not recorded. G. A. R. K.

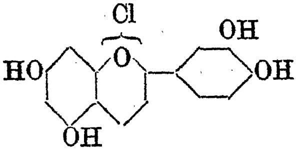
A Synthesis of Pyrylium Salts of Anthocyanidin Type. III. A New Synthesis of Pelargonidin Chloride. D. D. PRATT and R. ROBINSON (*J. Chem. Soc.*, 1924, **125**, 188—199).—Phloroglucinol dimethyl ether on treatment with formanilide and phosphoryl chloride, followed by subsequent decomposition, yields 2-hydroxy-4 : 6-dimethoxybenzaldehyde and a smaller relative amount of 4-hydroxy-2 : 6-dimethoxybenzaldehyde. When hydrogen chloride is passed into a cold solution of the 2-hydroxy-compound in the presence of ω-4-dimethoxyacetophenone, a good yield of tetramethylpelargonidin chloride (annexed formula) is obtained. On demethylation, pelargonidin chloride is produced. 4-Hydroxy-2 : 6-dimethoxybenzaldehyde on similar treatment gives a trimethylpelargonidin chloride. It is suggested that the blue coloration characteristic of pelargonidin and other anthocyanidins is dependent on the presence of at least four hydroxyl groups, as well as on their positions. 3 : 7-*Dihydroxy-2-phenylbenzopyrylium chloride* crystallises in orange-brown prisms, decomposing at 184°. 3 : 7 : 4'-*Trihydroxy-2-phenylbenzopyrylium chloride*, $C_{15}H_{11}O_4Cl,H_2O$, crystallises



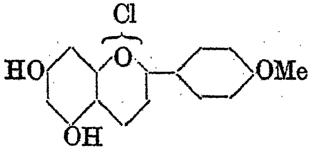
in needles, and decomposes at 262°. 4-*Hydroxy*-2 : 6-*dimethoxybenzaldehyde* crystallises in colourless prisms, m. p. 190°. *Trimethylgalangidin ferrichloride* (3 : 5 : 7-*trimethoxy*-2-*phenylbenzopyrylium ferrichloride*) forms yellowish-brown prisms, m. p. 174°. The *trimethylgalangidin chloride* crystallises in orange-red needles.

F. G. P.

A Synthesis of Pyrylium Salts of Anthocyanidin Type. IV. Flavylium Salts related to Chrysin, Apigenin, and Luteolin. D. D. Pratt, R. Robinson, and P. N. Williams (*J. Chem. Soc.*, 1924, **125**, 199—207; cf. previous abstract).—A series of compounds related to the flavones has been obtained and a system of nomenclature based on names suggesting their relationship to particular flavones and having the termination *-idin* suggested. Thus (I) is luteolidin chloride. The dimethyl ether of chrysinidin chloride is obtained by the action of hydrogen chloride on acetophenone in the presence of 2-hydroxy-4 : 6-dimethoxybenzaldehyde, and has been isolated as a ferrichloride. With phloroglucinol, *p*-anisyl β-hydroxyvinyl ketone reacts in the presence of hydrogen chloride to give acacetidin chloride (II). Trimethylapigenidin ferrichloride has been prepared from 2-hydroxy-4 : 6-dimethoxybenzaldehyde and acetylanisole. *Dimethylchrysinidin ferrichloride*, $C_{17}H_{15}O_3Cl_4Fe$, crystallises in reddish-brown prisms, m. p. 178°. p-*Anisyl β-hydroxyvinyl ketone*, $OMe\cdot C_6H_4\cdot CO\cdot CH{:}CH\cdot OH$, can be isolated as a *copper* salt, green prisms, m. p. 206—207°. 7-*Hydroxy*-4′-*methoxy*-2-*phenylbenzopyrylium chloride*, $C_{16}H_{13}O_3Cl,2H_2O$, brownish-orange needles, decomposes at 182—183°; its *picrate* melts at 219—221°. *Acacetidin chloride* forms brown prisms, m. p. >360°; *trimethylapigenidin ferrichloride*, orange needles; 2-*hydroxy*-4 : 6-*dimethoxystyryl* 3 : 4-*dimethoxyphenyl ketone*, yellow prisms, m. p. 178—179°; *tetramethyl-luteolidin ferrichloride*, salmon-red needles, m. p. 206—207°.



(I.)



(II.)

F. G. P.

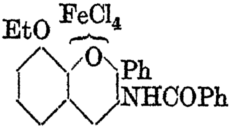
Some Derivatives of Benzopyrylium. R. Robinson and (in part) H. G. Crabtree, C. R. Das, W. Lawson, R. W. Lunt, B. H. Roberts, and P. N. Williams (*J. Chem. Soc.*, 1924, **125**, 207—214).—The oxonium salts described have been prepared by the method of synthesis, which depends on the condensation of a derivative of salicylaldehyde and a substance containing the group $-CO\cdot CH_2-$, under the influence of hydrogen chloride. 4-*Methoxyphenyl* 2-*hydroxy*-5-*methylstyryl ketone*,

$$OH\cdot C_6H_3Me\cdot CH{:}CH\cdot CO\cdot C_6H_4\cdot OMe,$$

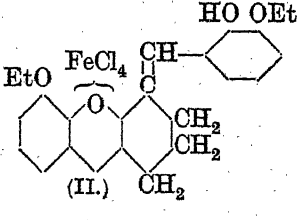
forms yellow plates, m. p. 151—152°; 4′-*methoxy*-2-*phenyl*-6-*methyl*-

benzopyrylium ferrichloride, $C_{17}H_{15}O_2Cl_4Fe$, obtained from the ketone, crystallises in crimson needles, m. p. 165—166°. *Phenyl 2-hydroxy-3-methoxystyryl ketone*, $MeO\cdot C_6H_3(OH)\cdot CH{:}CH\cdot COPh$, crystallises in yellow prisms, m. p. 112°. 8-*Methoxy-2-phenylbenzopyrylium ferrichloride*, from the ketone, crystallises in reddish-brown needles, m. .p. 157°. 8 : 4′-*Dimethoxy-2-phenylbenzopyrylium ferrichloride*, obtained from *o*-vanillin and *p*-methoxyacetophenone, crystallises in brown needles, m. p. 180°. 2 : 3 : 4-*Trimethoxyphenyl 2-hydroxy-3-methoxystyryl ketone*, obtained from *o*-vanillin and gallacetophenone trimethyl ether, forms bright yellow needles, m. p. 145°. 2′-*Hydroxy*-8 : 3′ : 4′-*trimethoxy-2-phenylbenzopyrylium ferrichloride* forms dark red needles, m. p. 194°; the *picrate*, red prisms, m. p. 164°; the *periodide*, purple needles, m. p. 133°; the *mercurichloride*, yellow needles, m. p. 143°. 2-*Phenyl*-3 : 4′-*dimethylbenzopyrylium ferrichloride*, from salicylaldehyde and *p*-tolyl ethyl ketone, forms yellow needles, m. p. 165—166°. 8-*Methoxy-2-phenyl*-3 : 4′-*dimethylbenzopyrylium ferrichloride* from *o*-vanillin and *p*-tolyl ethyl ketone, forms orange-brown needles, m. p. 172°; 8-*methoxy*-2-α-*naphthylbenzopyrylium ferrichloride*, from *o*-vanillin and α-naphthyl methyl ketone, brownish-red needles, m. p. 230°; 2′-*hydroxy*-3′-*methoxy-2-benzylidene*-1-*hydrindone*, from *o*-vanillin and α-hydrindone, yellow needles, m. p. 198°; 8-*methoxy*-2 : 3-*indeno*-(1 : 2)-*benzopyrylium ferrichloride*, red needles, m. p. 187—188°. F. G. P.

Some Benzopyrylium Salts. L. R. RIDGWAY and R. ROBINSON (*J. Chem. Soc.*, 1924, **125**, 214—222).—Attempts to prepare a benzopyrylium salt in which a halogen atom occurs in position 3 have not so far succeeded. The attachment of nitrogen to the pyrylium nucleus has been successful, and 3-benzoylamino-8-ethoxy-2-phenylbenzopyrylium ferrichloride (I) has been prepared from 2-hydroxy-3-ethoxybenzaldehyde and ω-benzoylaminoacetophenone. The removal of the benzoyl group from this salt was not possible. An account is included of some compounds which have been prepared in order to throw light on the property of fluorescence in relation to structure in this group. 8-*Ethoxy-2-phenylbenzopyrylium ferrichloride*, $C_{17}H_{15}O_2Cl_4Fe$, forms brown plates, m. p. 139—140°; 3-*benzoylamino*-8-*ethoxy*-2-*phenylbenzopyrylium ferrichloride* (I), orange-red needles, m. p. 198°; 3-*benzoylamino*-4′-*methoxy*-8-*ethoxy*-2-*phenylbenzopyrylium ferrichloride*, $C_{25}H_{22}O_4NCl_4Fe$, reddish-brown plates, m. p. 201°. 5-*Ethoxy*-4-(2-*hydroxy*-3-*ethoxybenzylidene*)-1 : 2 : 3 : 4-*tetrahydroxanthylium ferrichloride* (II) is obtained from cyclohexanone and 2-hydroxy-3-ethoxybenzaldehyde. It is a chocolate-coloured powder, m. p. 197°. The chloride obtained from this when boiled with water containing a

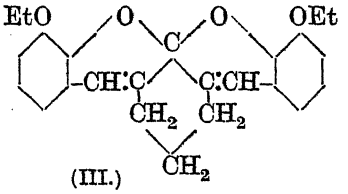


(I.)

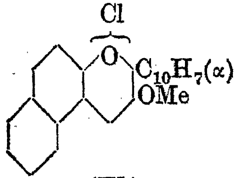


(II.)

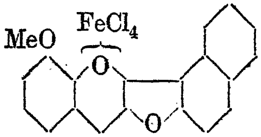
little hydrochloric acid is converted into *diethoxytrimethylenedibenzo-spiropyran* (III), colourless needles, m. p. 155°. *α-Naphthylmethoxymethyl ketone*, $C_{10}H_7\cdot CO\cdot CH_2\cdot OMe$, is obtained from methoxyacetonitrile and magnesium α-naphthyl bromide. It is a pale yellow, viscid oil, b. p. 184—186°/13 mm. It condenses with 2-hydroxy-5-methylbenzaldehyde to *3-methoxy-2-α-naphthyl-6-methylbenzopyrylium chloride*, $C_{21}H_{17}O_2Cl,3H_2O$, orange needles, m. p. 84°. The *ferrichloride* crystallises in plates, m. p. 184°. With 2-hydroxy-3-ethoxybenzaldehyde the above ketone yields *3-methoxy-8-ethoxy-2-α-naphthylbenzopyrylium chloride*, $C_{22}H_{18}O_3Cl,2H_2O$, orange-red plates, m. p. 115—116°, whilst with β-hydroxy-α-naphthaldehyde, *3-methoxy-2-α-naphthyl-naphtha-*(2 : 1)*-pyrylium chloride* (IV) is obtained in red, microscopic plates, m. p. 94°. The *ferrichloride* forms bright red plates, m. p. 183°. 6 : 4′*-Dimethoxy-2-phenylbenzopyrylium chloride* forms orange-red plates, m. p. 135°; the *ferrichloride* crystallises in brownish-red plates, m. p. 192—193°. 8-*Methoxy*-β-*naphthacoumarono*-(β : α-2 : 3)-*benzopyrylium chloride* (V) is prepared from *o*-vanillin and β-naphthacoumaranone. It crystallises in green prisms, m. p. 236—240°. When warmed with ethyl alcohol and a trace of sodium acetate, it is decolorised and the colourless *ethyl ether* of the pyranol is obtained in the form of needles, m. p. 165°.



(III.)

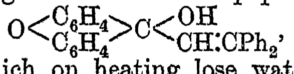
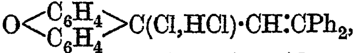
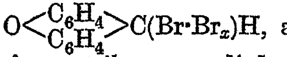
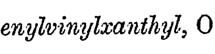


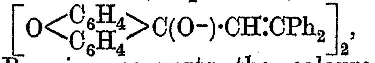
(IV.)



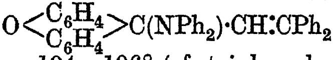
(V.)

F. G. P.

“ Tervalent ” Carbon. I. The Tetra-arylallyl Radicals and their Derivatives. K. Ziegler [with G. Bremer, F. Thiel, and F. Thielmann] (*Annalen*, 1923, **434**, 34—78; cf. A., 1922, i, 1047).—This investigation was undertaken to determine the factors responsible for the dissociation of poly-substituted ethane derivatives. For this purpose, compounds of the type of octaphenyldiallyl were studied. Assuming that the theoretical considerations developed by Thiele and Werner are correct, the unsaturated ββ-diphenylvinyl group would possess a markedly higher degree of “ valency requirement ” than the relatively saturated phenyl residue. Comparison of the dissociation capacity of the diallyl derivatives with that of the hexaphenylethanes provides a test for the accuracy of the theoretical considerations advanced by various authors. The first results of the work are given in an earlier paper (*loc. cit.*). 9-ββ-*Diphenylvinylxanthenol*,  $O<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>C<\genfrac{}{}{0pt}{}{OH}{CH:CPh_2}$, has now been obtained in needles which on heating lose water and pass into the allene derivative. Characteristic salts are obtained, particularly the *perchlorate,* as well as acid halogenides such as the *chloride-hydrochloride,*  $O<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>C(Cl,HCl)\cdot CH{:}CPh_2$, red needles, m. p. 156—157°, and the *bromide hydrobromide,* m. p. 130—131°; perhalogenides, namely, the *chloride tetrabromide* and *bromide tetrabromide,* reddish-brown powders, decomp. 123—124°, and 128—129°, respectively. Double salts of the xanthyl chloride are obtained by addition of heavy metal salts to solutions of the chloride hydrochloride in glacial acetic acid. The *zinc chloride* salt is a red, crystalline solid, decomposing at 165—166°. Hydrolysis of the salts regenerates the xanthenol, whilst tertiary amines such as pyridine and dimethylaniline convert them into the allene derivatives. Methyl and ethyl alcohols convert the hydrohalogenides into 9-*methoxy-* and 9-*ethoxy*-9-ββ-*diphenylvinylxanthen,* crystallising in needles, m. p. 133—134° and 136—137°, respectively. These ethers are readily decomposed by acids into alcohol and the coloured salts. The salts, particularly the chloride hydrochloride, dissolve in saturated alcoholic hydrogen chloride unaltered, and on reduction by zinc the parent substance, 9-ββ-*diphenylvinylxanthen,* has been obtained in large, colourless crystals, m. p. 164—165°. This has also been obtained from 9-xanthylacetic acid by the Grignard reaction. Aryl and alkyl derivatives of 9-ββ-diphenylvinylxanthen are obtained by the action of the Grignard reagent on the xanthyl salts, particularly on the perchlorate. The xanthen and its alkyl and aryl derivatives are easily reduced by hydriodic acid, the ββ-diphenylvinyl group probably being eliminated as αα-diphenylethane. 9-*Ethyl*-9-ββ-*diphenylvinylxanthen* crystallises in colourless crusts, m. p. 129—130°. These xanthens, when acted on by bromine, yield perbromides such as  $O<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>C(Br\cdot Br_x)H$, and brominated compounds of the type of αββ-*tribromo-αα-diphenylethane,* $Ph_2CBr\cdot CHBr_2$, m. p. 88—89°. Di-*p*-anisyl ketone and 2 : 4 : 4′-trimethoxybenzophenone, on treatment with the magnesium compound of ββ-diphenylvinyl bromide, yield alcohols, $(MeO\cdot C_6H_4)_2CR\cdot CH{:}CPh_2$ and $(MeO)_2C_6H_3(MeO\cdot C_6H_4)\cdot CR\cdot CH{:}CPh_2$, from which crystalline perchlorates may be prepared. The *trimethoxy*-compound forms fine red crystals yielding violet-red solutions. Pyridine converts it into 2 : 4 : 4′-trimethoxydiphenyl-γγ-diphenylallene, $(MeO)_2C_6H_3\cdot C(C_6H_4OMe){:}C{:}CPh_2$, colourless crystals, m. p. 134—135°. Tetraphenylpropene derivatives have been prepared, *ααγγ-tetraphenylallyl ethyl ether,* $Ph_2C(OEt)\cdot CH{:}CPh_2$, resulting from the action of alcoholic sulphuric acid on the corresponding alcohol. It forms colourless crystals, m. p. 106—107°. *Tetraphenylallyl perchlorate,* obtained from tetraphenylallyl alcohol, is an unstable, chocolate-brown powder, decomposing at 63—64°. On keeping, it is converted into the colourless 1 : 1 : 3-triphenylindene. Results show that the coloured compounds of the substituted tetra-allylallenes are true tetra-arylallyl salts, that tetra-arylallyl alcohols are pseudo-bases; the chlorides were not isolated, losing hydrogen chloride and giving tetra-allylallenes; these allenes readily add acid so as to form salts. Magnesium aryl haloids convert the xanthen perchlorate into the free *di*-9-ββ-*diphenylvinylxanthyl*,  $O{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C\cdot CH{:}CPh_2$, a colourless, crystalline powder, m. p. 144—145°, sparingly soluble in most reagents. This dissolves in benzene with a yellow colour, the solution becoming brown on warming, turning yellow again on cooling. Air completely decolorises the solution, a peroxide,



$$\left[O{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C(O-)\cdot CH{:}CPh_2\right]_2,$$

being obtained. Bromine converts the coloured solution into 9-ββ-diphenylvinylxanthyl bromide tetrabromide. Hydrazobenzene reduces it to 9-ββ-diphenylvinylxanthen (cf. triphenylmethyl). Sodium and potassium give coloured metal derivatives, the potassium derivative crystallising in the form of a copper-red sludge. Dry air decolorises the solutions of the alkali metal derivatives, water also decomposes them with production of the xanthen, whilst ethyl bromide converts them into the ethylxanthene. Tetraphenylhydrazine converts the free radical into 9-ββ-*diphenylvinylxanthyldiphenylamine*,  $O{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C(NPh_2)\cdot CH{:}CPh_2$, crystallising in colourless plates, m. p. 194—196° (cf. triphenylmethyl). These analogies with hexaphenylethane show that the xanthyl compound in solution exhibits radical dissociation. Molecular-weight determinations in naphthalene show that the xanthyl is decomposed to the extent of about 60% into 2 mols. of radical-like form. The free tetra-arylallyl radicals are also obtained by the decomposition of the corresponding perchlorates with the Grignard reagent. *Dianisyldiphenylallyl*, $(MeO\cdot C_6H_4)_2\cdot C\cdot CH{:}CPh_2$, crystallises in dark green plates, 2 : 4 : 4′-*trimethoxydiphenyl-γγ-diphenylallyl*,

$$(MeO)_2\cdot C_6H_3\cdot C(C_6H_4OMe)\cdot C\cdot CH{:}CPh_2,$$

is similar, but the colour is deeper. *ααγγ-Tetraphenylallyl*, the parent substance, is a green, crystalline powder, molecular-weight determinations in benzene showing a degree of dissociation of 80%. These three compounds are exceedingly stable. The corresponding peroxides are very unstable. The sodium compounds of the allyl radicals are readily converted into the corresponding propenes. In the triarylmethyl series, the union of the two benzene nuclei through oxygen opposes the association of the radicals, for 9-phenylxanthyl in naphthalene is present to the extent of about 50—70% in the unimolecular form and about 30—50% in the bimolecular form, whilst hexaphenylethane under like conditions is only dissociated to the extent of 15—25%. Tetraphenylallyl, on the other hand, in benzene solution at 4°, is present in the bimolecular form to the extent of at most 20%, whilst 9-ββ-diphenylvinylxanthyl in naphthalene at 80° is present perhaps to the extent of 40%; at 4°, therefore, it is still more strongly associated. If, according to Thiele and Werner, the high valency requirement of a residue is explained by its unsaturated character, based on the principle of a distribution of affinity, the existence of tetra-arylallyl radicals is a weighty argument in favour of this principle. αα-Diphenylethylene is essentially more unsaturated than benzene, so that it must be assumed that the ββ-diphenylvinyl residue requires more valency than the phenyl residue, and in agreement with this it is found that on replacing two phenyl residues in hexaphenylethane by two such residues the tendency to dissociate is very much increased.

F. G. P.

Atropine Phosphates. L. Debucquet (*J. Pharm. Chim.*, 1924, **29**, 15—22).—The salt $C_{17}H_{23}O_3N,H_3PO_4$ is obtained in 92% yield when an alcoholic solution containing equimolecular quantities of atropine and phosphoric acid is heated for half an hour in a water-bath at 90—95°, and then left to crystallise. Small, lustrous crystals (m. p. 196°) are obtained which are soluble in rather less than five times their weight of water (giving a solution acid to litmus), sparingly soluble in cold alcohol and almost insoluble in ether and chloroform. Attempts to prepare the salt, $(C_{17}H_{23}O_3N)_2,H_3PO_4$, gave only the monobasic phosphate (in diminished yield) and unchanged atropine. W. T. K. B.

Stereoisomerism and Local Anæsthetic Action in the β-Eucaine Group. Resolution of β- and *iso*-β-Eucaine. H. King (*J. Chem. Soc.*, 1924, **125**, 41—57).—On benzoylation, α- and β-vinyldiacetonalkamines yield *O*-benzoyl derivatives and for convenience the name of *iso*-β-eucaine is proposed for the derivative of the β-compound. β-Eucaine has been resolved by means of camphorsulphonic acid. With *d*-camphor-10-sulphonic acid, the partial racemate, dl-β-*eucaine* d-*camphor*-10-*sulphonate*, was obtained, working between the ordinary temperature and zero, and it has been found possible to resolve this salt by means of the more soluble active forms which are unstable in respect of the partial racemate, a total yield of 54% of l-β-*eucaine* d-*camphorsulphonate* being obtained. Owing to the formation of a continuous series of mixed crystals between the two active salts, the more soluble *d*-β-eucaine *d*-camphorsulphonate could not be isolated, but the isolation of d-β-*eucaine* l-*camphorsulphonate* was finally accomplished by the use of *l*-camphor-10-sulphonic acid. *iso*-β-Eucaine was resolved by the use of *d*-α-bromocamphor-π-sulphonic acid. In this case the salts, being of approximately equal solubility, separate alternately from the solution on fractional crystallisation. On the rabbit's cornea *r*-β-eucaine, *r*-*iso*-β-eucaine and their optically active components have approximately equal local anæsthetic action; on the sciatic nerve of the frog, however, β-eucaine is a more powerful anæsthetic than *iso*-β-eucaine. dl-β-*Eucaine* d-*camphorate* forms plates, m. p. 211—212°; the l-*malate* has m. p. 212—213° and $[\alpha]_D$ $-2{\cdot}6°$; the d-*tartrate* crystallises in tablets which have m. p. 257° and $[\alpha]_D$ $+10{\cdot}1°$. The *d*-camphor-10-sulphonate (mono-alcoholate) forms tablets, m. p. 228—229°, $[\alpha]_D$ $+10{\cdot}3°$ (anhydrous salt). *l*-β-Eucaine *d*-camphorsulphonate forms leaflets, m. p. 248—249°, $[\alpha]_D$ 4·78° and 4·83°, whence the *l*-β-eucainium-ion has $[\alpha]_D$ $-11°$. *d*-β-Eucaine *l*-camphorsulphonate has $[\alpha]_D$ $-5{\cdot}09°$, whence the *d*-β-eucainium-ion has $[\alpha]_D$ $+10{\cdot}6°$. l-β-*Eucaine* forms prisms, m. p. 57—58°. The *hydrochloride* forms plates (m. p. 244—245°, $[\alpha]_D$ −11·3°), the *picrate* (small prisms) having m. p. 198—199°. d-β-*Eucaine* has m. p. 57—58°, the *hydrochloride* having $[\alpha]_D$ +11·5°. r-β-*Eucaine hydrochloride* forms tablets, m. p. 277—279°; the free *base* has m. p. 70—71°; the *picrate* (plates), has m. p. 230·5—231·5°. d-α-*Vinyldiacetonalkamine hydrochloride* (tablets, m. p. above 300°), has $[\alpha]_D$ +13·3°; the l-*hydrochloride* has m. p. above 300° and $[\alpha]_{5461}$ −18·5°. The l-*base* forms prisms, m. p. 79—81° (*picrate*, needles, m. p. 242—244°). N-*Benzoyl*-β-*vinyldiacetonalkamine*, obtained by benzoylation of the β-alkamine base, forms leaflets, m. p. 121—122°; the O-*benzoyl* derivative, obtained by benzoylating the hydrochloride, forms needles or plates, m. p. 269—271°. Its *picrate* has m. p. 256—258°. l-iso-β-*Eucaine* d-α-*bromocamphor*-π-*sulphonate* forms needles, m. p. 236—238°, and has $[\alpha]_{5461}$ +52·1°, and $[M]_{5461}$ +290·9°, whence $[M]_{5461}$ for the *l-iso*-β-eucainium-ion is −55·6°. d-iso-β-*Eucaine* d-α-*bromocamphor*-π-*sulphonate* forms needles containing 0·5—1 mol. H_2O, the anhydrous salt having $[\alpha]_{5461}$ +70°, $[M]_{5461}$ +390°, whence the *d-iso*-β-eucainium-ion has $[\alpha]_{5461}$ +17·8°. d-iso-β-*Eucaine hydrochloride* forms needles, m. p. 271—273°, $[\alpha]_{5461}$ +14·9°. The l-*hydrochloride* has m. p. 271—273°, and $[\alpha]_{5461}$ −14·25°. The l-*picrate* forms needles, m. p. 280°. d-β-*Vinyldiacetonalkamine hydrochloride*, tablets, has m. p. 217—219°, $[\alpha]_{5461}$ +22·85°. The *base* has m. p. 121—123°; the *picrate* (needles) has m. p. 181—182°. ON-*Dibenzoyl*-α-*vinyldiacetonalkamine*, obtained by benzoylation of β-eucaine base, crystallises in plates, m. p. 142—143°. The similar *dibenzoyl* derivative from the *iso*-β-eucaine base forms prisms, m. p. 114—115°. F. G. P.

Complex Thiocyanates of Tervalent Metals. III. G. Scagliarini and G. Tartarini (*Gazzetta*, 1923, **53**, 876—878).—Unlike vanadium (A., 1923, i, 547, 1225), molybdenum forms complex thiocyanates which are highly stable and resemble, indeed, those of chromium.

Piperidine vanadihexathiocyanate, $(C_5H_{11}N{\cdot}H)_3[V(SCN)_6]$, forms deep red acicular crystals; *basic pyridine vanaditetrathiocyanate*, $(C_5H_5N{\cdot}H)_3\left[V\begin{matrix}(SCN)_4\\(OH)_2\end{matrix}\right]$, small, brick-red crystals; *hexamethylenetetramine molybdihexathiocyanate*, $(C_6H_{12}N_4{\cdot}H)_3[Mo(SCN)]_6$, straw-yellow crystals; *basic pyridine molybdipentathiocyanate*,

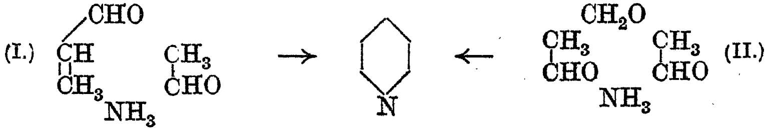
$$(C_5H_5N{\cdot}H)_3[Mo(SCN)_5OH],$$

orange-yellow crystals; and *basic piperidine molybdipentathiocyanate*, $(C_5H_{11}N{\cdot}H)_3[Mo(SCN)_5OH]$, brick-red crystals.

T. H. P.

Galegine. Barger and White.—(See i, 272.)

The Synthesis of Pyridine from Aldehydes and Ammonia. A. E. Tschitschibabin and (Mlle.) M. P. Oparina (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 601—606; cf. A., 1923, i, 1121 *et seq.*).—Pyridine can theoretically be formed by the interaction of ammonia either with one molecule of acraldehyde and one of acetaldehyde (scheme I) or with two molecules of acetaldehyde and one of formaldehyde (scheme II), thus:



Either scheme would account for the formation of small quantities of pyridine in the experiments of Stöhr (A., 1891, 579; 1892, 628), because it is well known that acraldehyde is formed from formaldehyde and acetaldehyde and that the process is reversible.

It is now shown that mixtures of acraldehyde and acetaldehyde or of acetaldehyde and ethylal can be made to react with ammonia under the influence of alumina (*loc. cit.*), yielding pyridine as the main product. In the former case, some β-picoline and a small quantity of α-picoline were also obtained, whilst in the second case α-, β-, and γ-picoline and 3 : 5-dimethylpyridine were isolated in small quantities. The formation of β-picoline from ethylal, acetaldehyde, and ammonia is doubtless due to the intermediate formation of acraldehyde, which then reacts with ammonia, whilst pyridine can be produced according to either scheme (I) or (II).

G. A. R. K.

4-Methyl-2-ethylpyridine. A. E. Tschitschibabin (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 607—610).—Pure γ-picoline, regenerated from its picrate, was heated with ethyl iodide in sealed tubes at 310—325° and the new base isolated in the form of its *picrate*, short yellow prisms, m. p. 120—121°; the *base*, regenerated from this picrate, boiled at 172° and was characterised by the formation of the *chloroplatinate*, short, sparkling, orange prisms, m. p. 176° (decomp.), and the *chloroaurate*, yellow prisms, m. p. 80°. The synthesis of 4-methyl-2-ethylpyridine has since been described by Eckert and Loria (A., 1918, i, 79), but the properties of the derivatives prepared by them differ somewhat from those given above.

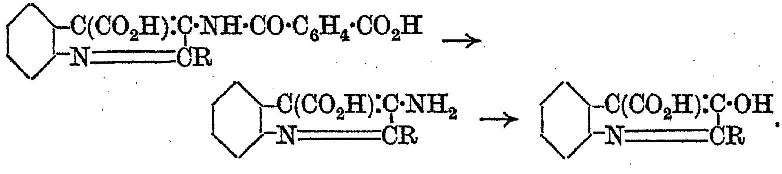
G. A. R. K.

The Condensation of Acetylene with Ammonia in the Presence of Alumina. A. E. Tschitschibabin and P. A. Moschkin (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 611—624).—A preliminary account of this work has already been published (A., 1915, i, 638); a detailed description is now given of the method of synthesis and of the separation of the pyridine bases formed by the fractional precipitation of their picrates. Pyrrole bases were found to be present; of the crude condensation product, some 30% consisted of picolines, which were isolated in the form of their picrates and, by crystallising the latter from acetone, were shown to consist of the α-compound with small quantities of the γ-isomeride. The collidine fraction constituted about 10% of the original mixture. The separation was again effected through the picrates, which were crystallised from ethyl acetate. The presence of β-collidine (4-methyl-3-ethylpyridine, chloroaurate, m. p. 140—141°, chloroplatinate, m. p. 215° [decomp.], picrate, m. p. 149°), identical with that obtained from cinchonine, and 2-methyl-5-ethylpyridine (picrate, m. p. 164°, chloroaurate, m. p. 88°) was confirmed. In addition, two other *collidines* were isolated, one of b. p. 178—182°/756·7 mm. (*picrate*, orange rods, m. p. 143°; *chloroaurate*, m. p. 119—121°; *chloroplatinate*, m. p. 207° [decomp.]), and another of b. p. 185·5—186·5°/756·7 mm. (*picrate*, short, flattened, orange needles, m. p. 134°; *chloroaurate*, plates, m. p. 116—118°; *chloroplatinate*, orange crystals, m. p. 210° [decomp.]). These collidines do not appear to be identical with 4-methyl-2-ethylpyridine (preceding abstract) or with either 2 : 3 : 4- or 2 : 3 : 6-trimethylpyridine which might possibly have been produced; but it is thought that the compounds may not be pure.

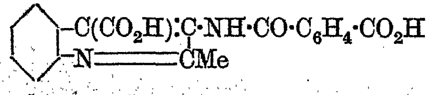
G. A. R. K.

The Absorption Spectra of some Indole Derivatives. F. W. Ward (*Biochem. J.*, 1923, **17**, 891—897).—Using the Hilger ultra-violet spectrum photometer, the absorption spectra of the following compounds have been charted : indole, indole-3-carboxylic acid, indole-3-aldehyde, indole-3-ethyl alcohol, indole-3-propionic acid, indole-3-alanine (tryptophane), 2 : 3-dihydroxyindole, 2-hydroxy-3-indole-aldehyde, isatin, and sodium indigotinsulphonate. The effect of substitution in the indole nucleus is discussed. J. P.

Certain Quinoline-4-carboxylic Acids. S. Berlingozzi and C. Marzella (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 403—406; cf. A., 1923, i, 482, 847).—The action of acetonyl- or phenacyl-phthalimide on isatoic acid gives rise, in the usual way, to compounds of the type :



When heated beyond their melting points, all these quinoline-4-carboxylic acids lose carbon dioxide, yielding the corresponding 3-amino- and 3-hydroxy-quinolines (*loc. cit.*). Those of the above acids which have a phenyl group in the 2-position may be regarded as derivatives of 2-phenylquinoline-4-carboxylic acid so largely used in therapeutics.



The *compound* (annexed formula) obtained from isatoic acid and acetonylphthalimide, crystallises in minute, white needles, m. p. 267—268° (decomp.).

3-*Amino-2-methylquinoline-4-carboxylic acid*, $C_{11}H_{10}O_2N_2$, obtained, together with phthalic acid, when the preceding compound is boiled with concentrated hydrochloric acid, forms lemon-yellow prisms, m. p. 232—233° (decomp.), yields solutions which develop fluorescence on addition of a mineral acid, and gives 3-amino-2-methylquinoline when heated at 233—235°. Its *acetyl* derivative forms a white, microcrystalline powder, m. p. 272—273°.

3-*Hydroxy*-2-*methylquinoline*-4-*carboxylic acid*, prepared by the action of nitrous acid on the preceding amino-compound, forms minute, pale yellow crystals, m. p. 229—230° (decomp.), and is converted into 3-hydroxy-2-methylquinoline when fused; its alcoholic solutions are fluorescent and are coloured red by ferric chloride.

The *compound* formed by condensation of isatoic acid with phenacylphthalimide crystallises in lustrous, straw-yellow scales, m. p. 260° (decomp.).

3-*Amino*-2-*phenylquinoline*-4-*carboxylic acid* forms pale yellow needles and prismatic plates, m. p. 226° (decomp.), exhibits fluorescence in acid solution, and gives 3-amino-2-phenylquinoline when heated. Its *acetyl* derivative crystallises in lustrous, white scales, m. p. 257—258°.

3-*Hydroxy*-2-*phenylquinoline*-4-*carboxylic acid* is obtained as a lemon-yellow, microcrystalline powder, m. p. 206—207°, forms fluorescent alcoholic solutions which are reddened by ferric chloride, and gives 3-hydroxy-2-phenylquinoline when heated. T. H. P.

The Absorption Spectra of Kynurenic Acid and some Related Quinoline Compounds. F. W. WARD (*Biochem. J.*, 1923, **17**, 903—906).—The absorption spectra of quinoline, quinaldine, lepidine, quinaldinic acid, 2 : 6-dimethylquinoline, kynurenic acid, and of quinolylacetaldehyde have been mapped. The last-mentioned compound gives an abnormal spectrum and doubts are expressed as to its constitution. The effects of substituents in the quinoline nucleus are discussed. J. P.

Some Heterocyclic Derivatives of Substituted *o*-Aminophenols. A. KORCZYNSKI and ST. OBARSKI (*Bull. Soc. chim.*, 1923, **33**, [iv], 1823—1832).—4-Chloro-2-nitrophenol, on electrolytic reduction, gave 4-*chloro*-2-*aminophenol* (m. p. 185°; *diacetyl* derivative, m. p. 201°). The following were prepared in a similar manner: 4-*chloro*-6-*bromo*-2-*aminophenol* (*acetyl* derivative, m. p. 150°), 4-bromo-2-aminophenol, 4 : 6-dibromo-2-aminophenol, and 4 : 6-di-iodo-2-aminophenol.

4-Chloro-2-aminophenol, on heating with acetamide (cf. Niementowski, A., 1898, i, 210) gave 4-*chloro*-1-*methylbenzoxazole* (m. p. 63°). The following compounds were obtained in a similar manner: 4-*bromo*-1-*methylbenzoxazole* (m. p. 70°), 4-*chloro*-6-*bromo*-1-*methylbenzoxazole* (m. p. 117°), and 5 : 6-*dibromo*-1-*methylbenzoxazole* (m. p. 127°). All the above oxazoles form yellow needles.

4-Chloro-2-aminophenol was converted (cf. Chetmicki, A., 1887, 477) by thiocarbonyl chloride, in presence of pyridine, into 4-*chloro*-1-*thiolbenzoxazole* (m. p. 283°), and the following compounds were prepared in a similar manner: 4-*chloro*-6-*bromo*-1-*thiolbenzoxazole* (m. p. 228°) and 4 : 6-*dibromo*-1-*thiolbenzoxazole* (m. p. 235°). All the above thiol derivatives form yellow needles, soluble in alkali.

4-Bromo-2-aminophenol (2 mols.) on boiling in alcoholic solution with chloroanil (1 mol.) affords 8-*bromo*-4-*aminophenoxazone* (giving a blue solution in concentrated sulphuric acid), the following compounds being similarly prepared: 8-*chloro*-2 : 10-*dibromo*-4-*aminophenoxazone* (reddish-violet solution in concentrated sulphuric acid), 2 : 8 : 10-*tribromo*-4-*aminophenoxazone*, and 2 : 8 : 10-*tri-iodo*-4-*aminophenoxazone* (blue solution in concentrated sulphuric acid). The above phenoxazones form red needles, not melting at 300°.

Chloroanil converts 4-nitro-2-aminophenol into a *substance* which forms orange-red needles. E. E. T.

Diphenylyl Phenylenediamines and the Colour of their Oxidation Products. J. Piccard and F. Abouchy (*Helv. Chim. Acta*, 1924, **7**, 75—83).—To compare the auxochromic effect of the diphenylyl group, $Ph\cdot C_6H_4-$, with those of phenyl and alkyl groups, the following derivatives of *p*-phenylenediamine were prepared, for oxidation into *meri*-quinonoid salts: *s*-di-*p*-diphenylyl-*p*-phenylenediamine (I); *s*-diphenyldi-*p*-diphenylyl-*p*-phenylenediamine (II), and tetra-*p*-diphenylyl-*p*-phenylenediamine (III). To prepare the first compound, (I), *p*-dibromobenzene was condensed with *p*-acetamidodiphenyl, giving s-*diacetyldi*-p-*diphenylyl*-p-*phenylenediamine*, colourless crystals, m. p. 245°. By alkaline hydrolysis this gave s-*di*-p-*diphenylyl*-p-*phenylenediamine*, long, colourless spangles, m. p. 256°. The second base, (II), was prepared in two ways, (*a*) by condensing (I) with iodobenzene, and (*b*) by condensing *p*-iododiphenyl with *s*-diphenyl-*p*-phenylenediamine. s-*Diphenyldi*-p-*diphenylyl*-p-*phenylenediamine* forms small crystals, m. p. 211°. The third base, (III), was also obtained in two ways, (*a*) by condensing (I) with *p*-iododiphenyl, and (*b*) by condensing *p*-di-iodobenzene with di-*p*-diphenylylamine. The product, *tetra*-p-*diphenylyl*-p-*phenylenediamine*, forms small, colourless crystals, m. p. 280°. Of these three bases, only the first can be oxidised to a quinonedi-imine. By oxidation with chromic acid, it gives *di*-p-*diphenylylbenzoquinonedi-imine*,

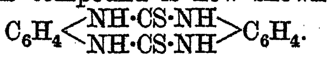
$$Ph\cdot C_6H_4N{:}C_6H_4{:}N\cdot C_6H_4\cdot Ph,$$

a red, amorphous powder, m. p. 266°. It is less basic than diphenylbenzoquinonedi-imine, and the colours of its salts are deeper; its mono-acid salts are blue, di-acid salts violet, and *meri*-quinonoid salts green. meri*Di*-p-*diphenylylbenzoquinonedi-imonium picrate*,

$$[Ph\cdot C_6H_4NH{:}C_6H_4{:}NH\cdot C_6H_4\cdot Ph{::::}Ph\cdot C_6H_4NH\cdot C_6H_4\cdot NH\cdot C_6H_4Ph][C_6H_2(NO_2)_3O]_2,$$

forms a bluish-green powder, m. p. 208°. A picrate of the *meri*-quinonoid salt of the second base was also isolated; it forms a yellowish-green powder, m. p. 169°. The colours of the *meri*-quinonoid salts of the three bases in solution are respectively bluish-green, green, and yellowish-green. The colours of the *holo*-quinonoid salts are only developed in concentrated sulphuric acid solution, and are respectively violet, bluish-violet, and blue. It is noted that glacial acetic acid dissolves the quinonedi-imine compounds as bases, the colour of the salts being developed only on addition of water. The leuco-compounds are weaker bases than the *holo*-quinonoid compounds, but the *meri*-quinonoid compounds are stronger bases than either of these. The auxochromic effect of the diphenylyl group in *meri*-quinonoid salts in the phenylenediamine, benzidine, or fuchsine series is less than that of two phenyl groups, but considerably greater than that of one group. The phenylated salts in the benzidine series are deeper in colour than the diphenylylated salts in the phenylenediamine series. The difference between the effect of the phenyl and diphenylyl groups is more marked in the *holo*-quinonoid than in the *meri*-quinonoid salts. It may be stated as a general rule that the weight of a group has more effect in the active chromophore than in an auxochromic group. E. H. R.

The Reaction of Carbon Disulphide on *p*-Phenylenediamine.

C. E. Bolser and E. B. Hartshorn (*J. Amer. Chem. Soc.*, 1923, **45**, 2349—2355).—When *p*-phenylenediamine and carbon disulphide are boiled in alcoholic solution (Pawlewski, A., 1899, ii, 405), a small quantity of *pp'*-diaminodiphenylthiocarbamide is produced, together with an insoluble compound, which has been described as *p*-phenylenethiocarbamide, $C_6H_4{<}^{NH}_{NH}{>}C{:}S$ (Lellmann, A., 1883, 185). This compound is now shown to be *di*-p-*phenylenedithiocarbamide*,  $C_6H_4{<}^{NH\cdot CS\cdot NH}_{NH\cdot CS\cdot NH}{>}C_6H_4$. In the first place, its formation may be almost entirely suppressed, the yield of diaminodiphenylthiocarbamide being correspondingly increased, by conducting the process in aqueous solution, by keeping the temperature of reaction low, and by decreasing the concentration of carbon disulphide. It is advisable frequently to remove, by filtration, the diaminodiphenylthiocarbamide, which is less soluble in warm alcohol than in hot, and still less soluble in water. This suggests that the simple thiocarbamide is an intermediate stage in the formation of the insoluble compound; that this is actually so is shown by the formation of the latter when carbon disulphide and *pp'*-diaminodiphenylthiocarbamide react in boiling alcoholic solution. The identity of the product with that formed directly from carbon disulphide and *p*-phenylenediamine is shown (although in neither reaction is an absolutely pure substance obtained) by the temperature of decomposition (285°), by the formation of *p*-phenylenediamine by the action of hot, concentrated acids, and by the formation of *p*-phenylenedithiocarbimide by the prolonged action of boiling acetic anhydride. The latter reaction proves that the compound has the above structure, since *p*-phenylenethiocarbamide could not give the dithiocarbimide, but should be converted into p-*acetamidophenylthiocarbimide*, white needles, m. p. 195—196°. The latter is produced by the action of boiling acetic anhydride on *di*-p-*acetamidophenylthiocarbamide*, a white solid, m. p. 235—237°, which is formed by the action of an excess of carbon disulphide on *p*-aminoacetanilide in boiling alcoholic solution. It was hoped that the hydrolysis of this derivative, which requires the use of hot, concentrated hydrochloric acid, might give di-*p*-aminophenylthiocarbamide (thus avoiding the concurrent formation of the insoluble compound), but actually phenylenediamine hydrochloride is the sole product.

The reduction, by means of stannous chloride and a mixture of glacial acetic acid and concentrated hydrochloric acid, of *azobenzene*-p-*thiocarbimide*, $Ph\cdot N{:}N\cdot C_6H_4\cdot NCS$, salmon-coloured needles, m. p. 94—95°, which is obtained by heating thiocarbonyl chloride and *p*-aminoazobenzene in carbon tetrachloride solution at 100°, gives diphenylenedithiocarbamide, but the latter does not appear until the solution is made alkaline. It is probable that the acid solution contains, in equilibrium with the dimeric compound, *p*-aminophenylthiocarbimide (hydrochloride). In fact, when the acetyl derivative (above) of the latter compound is boiled with glacial acetic acid, in the presence of this weaker acid diphenylenedithiocarbamide is precipitated, more of the same material being thrown down on dilution. It is evident that the tendency to the formation, by what is practically a tautomeric change, of this substance is so great, that free *p*-aminophenylthiocarbimide cannot exist, but, on liberation from its salts, immediately undergoes polymerisation. W. S. N.

New Methods of Splitting Pyrimidines. III. The Action of Iodine Solution on Pyrimidines. L. W. BASS and O. BAUDISCH (*J. Amer. Chem. Soc.*, 1924, **46**, 181—183; cf. A., 1922, ii, 328).—Pyrimidines with unsubstituted nitrogen atoms and with a double bond between carbon atoms 4 and 5 absorb iodine from solution in the presence of sodium bicarbonate. On distillation of the reaction mixtures, after removal of excess iodine, carbamide is found in the residues as a scission product. No carbamide can be detected before the distillation. Substitution by an alkyl group in position 5 retards the rapidity of decolorisation of iodine solution. Hydrouracil decolorises iodine solution, but no carbamide is formed when the reaction mixture is distilled. 1 : 3-Dimethylthymine does not decolorise iodine solution. Thymine itself yields carbamide and acetol; no pyruvic acid is formed. When bromine is substituted for iodine, the pyrimidine ring is not split under the conditions of the experiments. F. A. M.

New Methods of Splitting Pyrimidines. IV. A Study of the Mechanism of the Decomposition of Thymine. O. BAUDISCH and L. W. BASS (*J. Amer. Chem. Soc.*, 1924, **46**, 184—189; cf. preceding abstract).—The action of various oxidising agents on thymine has been studied; the primary products of the reactions still contain the carbamide residue. The final products, carbamide, acetol, and pyruvic acid, are formed only when the primary products are heated in aqueous solution with sodium hydrogen carbonate. Acetol is formed as a direct hydrolytic product of thymine, whilst pyruvic acid is formed by the complete hydrolysis of an intermediate oxidation product. A mechanism is suggested to explain the decomposition of thymine under the conditions used. F. A. M.

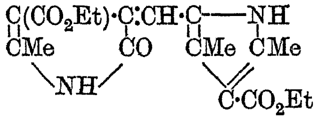
New Methods of Splitting Pyrimidines. V. The Action of Oxygen plus Ferrous Salts on Thymine under the Influence of Light. L. W. Bass (*J. Amer. Chem. Soc.*, 1924, **46**, 190—192; cf. preceding abstracts).—When in an atmosphere of oxygen aqueous solutions of thymine are illuminated using a quartz mercury arc, the pyrimidine is split to some extent into carbamide and pyruvic acid; no acetol is formed. The reaction is accelerated, but otherwise not affected, by ferrous sulphate or, to a smaller extent, by potassium ferrocyanide. No scission occurs in an atmosphere of nitrogen even in the presence of the above salts. F. A. M.

Catalysis. III. Reduction of Uracil to Hydrouracil. E. B. Brown and T. B. Johnson (*J. Amer. Chem. Soc.*, 1923, **45**, 2702—2708; cf. A., 1921, i, 806; 1922, i, 709).—Further experimental details are given, relating to the reduction of uracil to hydrouracil by means of hydrogen, in the presence of colloidal platinum. Colloidal palladium may also be used. Sulphur compounds, even when present only as traces, completely inhibit the reaction, but the chlorides of sodium, potassium, calcium, and magnesium are quite without effect. W. S. N.

Synthetic Researches on the Constitution of Bile-pigments. II. H. Fischer and J. Müller (*Z. physiol. Chem.*, 1924, **132**, 73—103).—If dry ammonia is passed through a cold alcoholic solution of ethyl α-acetyl-β-methylsuccinate, crystals are obtained, m. p. 77° (decomp.), apparently of ethyl β-amino-Δ^{β}-pentene-γδ-dicarboxylate, which on keeping or on warming in a vacuum at 40—50° completely change into ethyl 2-hydroxy-3 : 5-dimethylpyrrole-4-carboxylate, m. p. 127°, a compound which is also found in the mother-liquors from the crystals. This pyrrole derivative, when warmed in 50% sulphuric acid, yields α-methyl-lævulic acid, and when treated with hydrazine hydrate, is converted into the *hydrazide* of 2-hydroxy-3 : 5-dimethylpyrrole-4-carboxylic acid, sharp-angled leaflets, decomposing at 212°. This compound may be converted by nitrous acid into the *azide* of 3 : 5-dimethyl-2-hydroxypyrrole-4-carboxylic acid, flat prisms, which decompose explosively at 114°, and this compound, in solution in boiling absolute ethyl alcohol, yields *ethyl* 2-*hydroxy*-3 : 5-*dimethylpyrryl*-4-*carbamate*, white needles, decomposing at 148°, whilst if methyl alcohol is used, the corresponding *methyl carbamate* is obtained as white, glistening needles, decomposing at 164°. From ethyl acetylsuccinate, the following corresponding series of compounds is obtained: *ethyl* β-*amino*-Δ^{β}-*butene*-γδ-*dicarboxylate*, m. p. 122—124° (decomp.); ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate, m. p. 134°; (*hydrazide*, leaflets, decomposing at 232°; *azide*, needles, which decompose explosively at 135°; *methyl carbamate*, needles, m. p. 175°).

Ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate condenses with aldehydes in alcoholic solution in presence of hydrochloric acid, and the following compounds are described: *ethyl* 2-*keto*-3-*benzylidene*-5-*methyl*-2 : 3-*dihydropyrrole*-4-*carboxylate*, yellow leaflets,

m. p. 184°; *ethyl* 2-*keto*-3-p-*dimethylaminobenzylidene*-5-*methyl*-2 : 3-*dihydropyrrole*-4-*carboxylate*, red needles from alcohol, m. p. 231° (*hydrochloride*, yellow needles, unstable in air, decomposing at 210°, *perchlorate*, yellow needles, stable in air, m. p. 150° [decomp.]); *ethyl* 2-*keto*-3-o-*nitrobenzylidene*-5-*methyl*-2 : 3-*dihydropyrrole*-4-*carboxylate*, felted yellow needles, m. p. 201°; 4-*carbethoxy*-2-*hydroxy*-5-*methylpyrrolidyl*-3′-*carbethoxy*-2′ : 4′-*dimethylpyrrylmethene* (annexed formula), orange-yellow prisms, m. p. 210°, with which is also formed a *compound* (deep orange-yellow prisms, m. p. 162—163°); and 4-*carbethoxy*-2-*hydroxy*-5-*methylpyrrolidyl*-5′-*carbethoxy*-2′ : 4′-*dimethylpyrrylmethene*, needles, m. p. 266°.

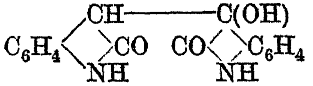


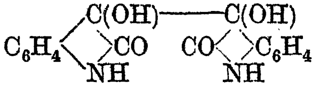
Ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate couples with benzene-diazonium chloride to give a *dye*, $C_{14}H_{15}O_3N_3$ (glistening, pure yellow, felted needles, m. p. 233°), which forms a *sodium* salt, $C_{14}H_{14}O_3N_3Na$, red needles, and a *potassium* salt, orange-yellow needles. When treated with ammoniacal copper solution the dye is converted into an isomeric *compound* (large orange-red to dark red, transparent needles, decomposing at 213°), which on crystallisation from alcohol yields the original dye. The latter, when reduced with zinc dust in hot alcoholic solution or with hydrogen in presence of platinum black, yields ethyl 3-amino-2-hydroxy-5-methylpyrrole-4-carboxylate, m. p. 244° (cf. Fischer and Herrmann, A., 1922, i, 1054). *Dyes* obtained similarly from *m*-nitrobenzene-diazonium chloride and from α-naphthalene-diazonium chloride, form thin, yellow, bunched needles, m. p. 233°, and red needles, decomposing at 234°, respectively. The application of the Gattermann reaction to ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate yields, besides a *by-product* which decomposes at 262°, the *aldimine*, $C_9H_{12}O_3N_2$, colourless leaflets, m. p. 241°, which is not hydrolysed by water to the aldehyde, and is decomposed by alkalis with the liberation of ammonia. The *aldehyde*, however, may be obtained when sodium is added to a boiling mixture of ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate and ethyl formate, and forms large, flat needles, m. p. 206°. It yields a *semicarbazone*, bunched needles, m. p. 252° (with previous browning and sintering), and a *hydrazone*, small rods, m. p. 190°. It condenses with ethyl 3-hydroxy-5-methylpyrrole-4-carboxylate to yield 4-*carbethoxy*-3-*hydroxy*-5-*methylpyrrolidyl*-4′-*carbethoxy*-2′-*hydroxy*-5′-*methylpyrrylmethene*, yellow needles, m. p. 250°, and with ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate to yield bis-(4-*carbethoxy*-2-*hydroxy*-5-*methylpyrryl*)*methene*, brownish-yellow prisms, m. p. 254°. 4-*Carbethoxy*-3-*hydroxy*-5-*methylpyrrole*-2-*aldehyde*, faintly coloured needles, m. p. 188°, is obtained when ethyl 3-hydroxy-5-methylpyrrole-4-carboxylate is condensed with ethyl formate in presence of sodium. Ethyl oxalate, similarly, condenses with ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate to form *ethyl* 4-*carbethoxy*-2-*hydroxy*-5-*methylpyrryl*-3-*glyoxylate*, glistening prisms, m. p. 180°, and with ethyl 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate to yield *ethyl* 5-*carbethoxy*-2 : 4-*dimethyl*-

pyrryl-3-ethanonoxalate, fine, colourless, felted needles, m. p. 150·5°. The latter is readily decomposed by alkalis to yield 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate, and forms a *semicarbazone*, m. p. 201°, and a *ketazine-hydrazide*, $C_{13}H_{17}O_3N_5$, needles, m. p. 239° (decomp.). Ethyl 2 : 4-dimethylpyrryl-3-ethanonoxalate forms a *semicarbazone*, m. p. 198° (decomp.). Ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate, when heated with hydrazine hydrate at 200° in a closed tube, yields 2 : 4-dimethylpyrrole. If 1′-*p*-toluoyl-4-carbethoxy-3-hydroxy-5-methylpyrrolidyl-3′-carbethoxy-2′ : 5′-dimethylpyrrylmethene is treated with benzene-diazonium chloride, decomposition of that compound takes place simultaneously with coupling to give a mixture of 3-carbethoxy-2 : 5-dimethyl-1-*p*-toluylpyrrole-4-aldehyde and 2-benzeneazo-4-carbethoxy-3-hydroxy-5-methylpyrrole. W. O. K.

Oxidation–Reduction. IV. Electrode Potentials of Indigotinsulphonates. M. X. SULLIVAN, B. COHEN, and W. M. CLARK (*U.S. Public Health Repts.*, 1923, **38**, 1669—1718).—A survey of the literature shows conflicting statements regarding the behaviour of indigotin and its sulphonates in vitro and in vivo, and a lack of satisfactory theories due to lack of quantitative data for the oxidation–reduction equilibrium. Indigotin-mono-, -di-, -tri-, and -tetra-sulphonates were prepared by Bloxam's method (A., 1906, ii, 819), and the electrode potentials at 30° were determined by elaboration of methods already described (A., 1923, ii, 726, etc.). The experimental results were in accord with the rational equation : $E_h = E_o - [(RT/nF)\log_e(S_r/S_o)] + (RT/nF)\log_e[K_1(H^+) + (H^+)^2]$, where E_h is the observed electrode potential referred to the hydrogen standard, S_r and S_o are the concentrations of total reductant and total oxidant, (H^+) is the hydrogen-ion concentration of the solution, and K_1 the acid dissociation constant of one of the two hydrogen atoms of the hydrogenated leuco-compound (dissociation of the sulphonic acids not being considered). The number, *n*, of electrons in the reversible oxidation–reduction is 2. The second acidic hydrogen atom of the leuco-compound has a dissociation constant below 10^{-12}. The values of E_o and K_1 were as follows : indigotin-monosulphonate $\rightleftharpoons$ leuco-compound, +0·262, $1·6\times10^{-8}$; indigotin-disulphonate $\rightleftharpoons$ leuco-compound, +0·291, $4·9\times10^{8}$; indigotintrisulphonate $\rightleftharpoons$ leuco-compound, +0·332, $7·7\times10^{-8}$; indigotintetrasulphonate $\rightleftharpoons$ leuco-compound, +0·365, $11·2\times10^{-8}$. Indigotin $\rightleftharpoons$ indigo-white is not adapted to accurate experiments in aqueous solution. Approximate data indicate $K_1=10^{-8}$ and E_o near that of the monósulphonate. Anomalies with borate buffers are shown, and evidence is given of a " salt effect " with other buffer systems, of the acidic nature of the leuco-compounds, and of the ionisation of only one hydrogen atom at moderate alkalinities. An electrometric method of analysis of mixtures of the sulphonates is developed. The data cover all conditions for the reversible oxidation–reduction of an indigotinsulphonate and give their properties for use in colorimetric determinations of oxidation–reduction intensities of biological solutions. CHEMICAL ABSTRACTS.

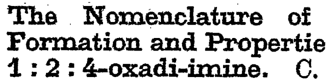
Constitution of Isatan and Isatide. A. Wahl and W. Hansen (*Compt. rend.*, 1924, **178**, 393—396; cf. following abstract).—Isatan (I), $C_{16}H_{12}O_3N_2$, on heating in boiling naphthalene solution, affords indine (cf. Laurent, *Ann. Chim. Phys.*, 1840, [iii], **3**, 469); it results from the condensation of oxindole and isatin in presence of piperidine (cf. Stollé, A., 1914, i, 992), and is the product called isatide by Erdmann (*J. pr. Chem.*, 1840, [i], **24**, 1), who treated isatin with excess of ammonium hydrosulphide. Isatan was obtained by Laurent (*loc. cit.*) by reducing disulphoisatide with ammonium hydrogen sulphite. Isatide, $C_{16}H_{12}O_4N_2$ (II), which does not give indine on heating, is the product obtained by Laurent by treating isatin with a slight excess of ammonium hydrosulphide, and by Heller (A., 1904, i, 416) by reducing isatin with zinc and acetic acid. Isatide is formed rapidly when a mixture of dioxindole and isatin is treated, in alcoholic solution, with piperidine.

(I.) 

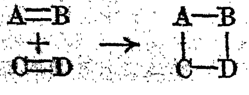
 (II).

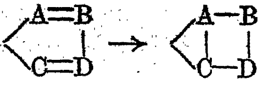
E. E. T.

Transformation and Constitution of Disulphoisatide. A. Wahl and W. Hansen (*Compt. rend.*, 1924, **178**, 214—216).—The formula, $C_{16}H_{12}O_2N_2S_2$, given by Laurent (*Ann. Chim. Phys.*, 1840, [iii], **3**, 469) to disulphoisatide has been confirmed. The formation of indine by the action of alkali on disulphoisatide is shown to depend on the nature and concentration of the alkali used, and not to occur if air is excluded. The conversion is best effected by adding aqueous sodium carbonate to an aqueous-alcoholic solution of disulphoisatide. Isatin is produced simultaneously (55% of that obtainable on the basis of the equation : $2C_{16}H_{12}O_2N_2S_2 + 2H_2O = C_{16}H_{10}O_2N_2 + 4H_2S + 2C_8H_5O_2N$). Sulphur is initially formed, and reduces indine to leuco*iso*indigotin, which is oxidised if air is present. The annexed formula (cf. Kohn and Ostersetzer, A., 1916, i, 607, and Lefèvre, *ibid.*, 430) is proposed for disulphoisatide, a disulphide formula being excluded, since on reduction it gives leuco*iso*indigotin (A., 1923, i, 607). E. E. T.

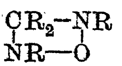


The Additive Formation of Four-membered Rings. III. The Nomenclature of Four-membered Rings and the Formation and Properties of some Derivatives of Methylene-1 : 2 : 4-oxadi-imine. C. K. Ingold (*J. Chem. Soc.*, 1924, **125**, 87—102).—It has been found that the formation of a four-membered ring, by the additive union of double bonds (I) is of considerable generality, and this confirms the prediction (T., 1922, **121**, 2793) made from the analogy with the tautomeric change or internal addition reaction shown in (II):

(I.) 

 (II.)

A system of nomenclature is proposed for the new heterocyclic ring types that have been already produced. Part of the object of the work is to discover which of these types are the most stable. It has been shown earlier (*loc. cit.*, and T., 1923, **123**, 2745) that certain types of azomethines and nitroso-compounds pass into stable cyclic bimerides. It is now shown that an azomethine and a nitroso compound of the particular type combine additively to give a stable 1 : 2 : 4-oxadi-imine (annexed formula).



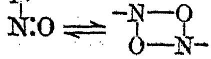
$\begin{array}{l}CR_2-NR\\ \,|\qquad\ \ |\\ NR-O\end{array}$

Methylene-p-*chloroaniline*, $CH_2{:}N{\cdot}C_6H_4Cl$, forms needles, m. p. 142°, the corresponding p-*bromo*-derivative, needles, having m. p. 169°. p-*Chloronitrosobenzene* has m. p. 90°, the corresponding *bromo*-derivative having m. p. 94°. The following compounds are also described: 2-*phenyl*-4-p-*tolylmethylene*-1 : 2 : 4-*oxadi-imine* (needles, m. p. 150°); the similar 4-p-*chlorophenylmethylene* compound (needles, m. p. 162°); the 4-p-*bromophenyl* compound (needles, m. p. 171°); 4-p-*chlorophenyl*-2-p-*tolylmethylene-oxadi-imine* (needles, m. p. 163°); the 4-p-*bromophenyl* derivative (m. p. 158°), the 2 : 4-*dichloro*-derivative (m. p. 171°), and the 2 : 4-*dibromo*-derivative (m. p. 175°). p-*Chlorophenylcarbylamine* forms needles (m. p. 71°), the corresponding *bromocarbylamine* having m. p. 99°. Both have an odour somewhat less powerful than that of phenylcarbylamine itself, but the taste of the vapour is considerably stronger. 2-p-*Chlorophenyl*-4-p-*bromophenylmethylene*-1 : 2 : 4-*oxadi-imine* forms needles, m. p. 171°.

Phenyl-p-*tolylcarbodi-imide*, $C_6H_4Me{\cdot}N{:}C{:}NPh$ (b. p. 170/12° mm.) (converted by aqueous-alcoholic hydrochloric acid into phenyl-*p*-tolylcarbamide), *phenyl*-p-*chlorophenylcarbodi-imide* (b. p. 175/11° mm.). p-*bromodiphenylcarbodi-imide* (b. p. 185/11° mm.), p-*chlorophenyl*-p-*tolylcarbodi-imide* (b. p. 175°/10 mm.), p-*bromophenyl*-p-*tolylcarbodi-imide* (b. p. 188°/10 mm.), pp′-*dichlorodiphenylcarbodi-imide* (b. p. 190°/10 mm.), pp′-*dibromodiphenylcarbodi-imide* (b. p. 202°/10 mm.), and p-*chloro*-p′-*bromodiphenylcarbodi-imide* (b. p. 198—200°/11 mm.) are, like the phenyl-*p*-tolyl derivative, viscous liquids, their constitutions being proved by conversion into the corresponding carbamides.

p-*Chlorophenyl*-p-*tolylcarbamide* (needles, m. p. 297—299° [decomp.]), p-*bromophenyl*-p-*tolylcarbamide* (needles, m. p. 316—318° [decomp.]), and p-*chloro*-p′-*bromodiphenylcarbamide* (needles, m. p. about 300° [decomp.]) were obtained (see *ante*) from the corresponding carbodi-imides. F. G. P.

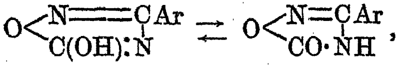
The Additive Formation of Four-membered Rings. IV. The Influence of Temperature on the Tendency towards Self-addition of the Nitroso-group. C. K. INGOLD and H. A. PIGGOTT (*J. Chem. Soc.*, 1924, **125**, 168—176).—Owing to the chromophoric character of the nitroso-group, the use of the colorimeter enables the reversible reaction



$2\,\overset{|}{N}{:}O \rightleftharpoons \begin{array}{l}-N-O\\ \ \ |\qquad|\\ \ \ O-N-\end{array}$

to be followed in greater detail than is the case with the reactions previously studied (see preceding abstract). The influence of temperature on the equilibrium is determined for the case of nitrosomesitylene in benzene solution. Using these results, the order of the reaction is calculated from certain equations, and shown to be in accordance with the chemical evidence. Nitrosomesitylene, the preparation of which (and of mesidine) from dimethylaniline is described, has m. p. 122—123° (cf. Pechmann and Nold, A., 1898, i, 310). The heat absorbed during the dissociation of 1 g.-mol. of dimeric nitrosomesitylene is calculated to be about 13,700 g.-cal. In 3% solution in benzene, dissociation occurs to the extent of about 18%; in a 2% solution, 21·6%. This corresponds with a molecular weight 245, agreeing fairly well with Bamberger's value 246 obtained (A., 1901, i, 141) cryoscopically in benzene solution. F. G. P.

Dioximes. XVII. G. PONZIO and B. ZANARDI-LAMBERTI (*Gazzetta*, 1923, **53**, 818—824).—In some of their properties, 5-hydroxy-3-aryl-1 : 2 : 4-oxadiazoles (or hydroxyazoximes),

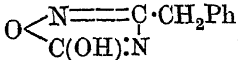


$$O<\begin{matrix}N{=\!=}CAr\\ C(OH){:}N\end{matrix} \rightleftharpoons O<\begin{matrix}N{=}CAr\\ CO\cdot NH\end{matrix},$$

which are formed by withdrawal of two atoms of hydrogen from the α-modifications of monoarylglyoximes, differ considerably from the 3 : 5-diaryl-1 : 2 : 4-oxadiazoles (or azoximes), which result on elimination of a molecule of water from a *s*-diarylglyoxime. Thus, the azoximes are either completely destroyed or slowly converted into nitriles by the action of reducing agents, whereas the hydroxyazoximes are very easily reduced to amidines, $NH_2{\cdot}CR{:}NH$, by means of hydriodic acid in presence of red phosphorus. Further, the hydroxyazoximes exhibit acid properties, the mean values of the ionisation constant at 25° being $0{\cdot}879\times10^{-5}$, $0{\cdot}022\times10^{-5}$, and $0{\cdot}140\times10^{-5}$ for 5-hydroxy-3-phenyl-, *p*-tolyl-, and benzyl-1 : 2 : 4-oxadiazoles; thus, the *p*-tolyl compound is slightly weaker than carbonic acid, and the other two compounds are stronger.

Benzenylamidine, obtained by reduction of 5-hydroxy-3-phenyl-1 : 2 : 4-oxadiazole, gives a picrate, m. p. 235°; Dieckmann (A., 1892, 705) gave m. p. 228°. According to Pinner ("Die Imidoaether," 167), 2 : 4 : 6-triphenyl-1 : 3 : 5-triazine is formed when benzenylamidine hydrochloride is heated for six hours at 120—140° with benzoyl chloride. This reaction occurs at the ordinary temperature when benzenylamidine carbonate is treated with 20% sodium hydroxide solution and benzoyl chloride.

5-Hydroxy-3-*p*-tolyl-1 : 2 : 4-oxadiazole, prepared from *p*-tolenylamidoxime and ethyl chlorocarbonate (cf. Schubart, A., 1890, 47), is the product of the isomerisation of the oxide of *p*-tolyl cyanide oxime (cf. Avogadro, this vol., i, 294). By hydriodic acid and red phosphorus it is converted into *p*-tolenylamidine, which forms a *picrate*, $C_6H_4Me{\cdot}C({:}NH){\cdot}NH_2,C_6H_3O_7N_3$, crystallising in yellow needles, m. p. 224—225° (decomp.), and a *carbonate*, crystallising in white laminæ, m. p. 127—128° (gas); the corresponding nitrate was described by Pinner (*loc. cit.*, 184). 5-Hydroxy-3-*p*-tolyl-1 : 2 : 4-oxadiazole forms the following derivatives: *sodium* salt, white powder; *silver* salt, white crystals, stable towards light; *methyl ether*, slender, white needles.

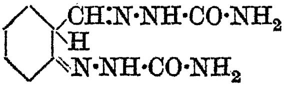
5-*Hydroxy*-3-*benzyl*-1 : 2 : 4-*oxadiazole*, 
$$O<\begin{matrix}N{=\!=\!=}C\cdot CH_2Ph\\ C(OH){:}N\end{matrix}$$
, prepared by the action of sodium hydroxide on the ethyl phenylethenylamidoximecarboxylate obtained by the interaction of ethyl chlorocarbonate and phenylethenylamidoxime, $CH_2Ph\cdot C(:NOH)\cdot NH_2$, crystallises in large, lustrous laminæ, m. p. 115°. By hydriodic acid and red phosphorus it is converted into phenylethenylamidine, $CH_2Ph\cdot C(:NH)\cdot NH_2$, the *picrate* of which forms yellow needles, m. p. 224° (decomp.). 5-Hydroxy-3-benzyl-1 : 2 : 4-oxadiazole forms a *sodium* salt, white powder; an insoluble *silver* salt, white, crystalline powder, stable towards light, and a *methyl ether*, crystallising in needles, m. p. 112—113°.

5-Hydroxy-3-α-naphthenyl-1 : 2 : 4-oxadiazole has m. p. 196°, and not 189° as stated by Richter (A., 1890, 62). α-*Naphthenylamidine*, $C_{10}H_7\cdot C(:NH)\cdot NH_2$, crystallises in white laminæ, m. p. 154°, and its *picrate* in yellow needles, m. p. 223° (decomp.).

5-Hydroxy-3-β-naphthenyl-1 : 2 : 4-oxadiazole, m. p. 219—220° (Richter, *loc. cit.*, gave 216°), yields on reduction β-naphthenylamidine, the *picrate* of which forms reddish-yellow needles, m. p. 240° (decomp.). T. H. P.

Tetrahydroindazoles. K. von Auwers, W. Buschmann, and R. Heidenreich (*Annalen*, 1924, **435**, 277—321).—A study of the tetrahydroindazoles obtained by condensing hydrazine derivatives with hydroxymethylene*cyclo*hexanone and 1-methyl-3-hydroxymethylene*cyclo*hexan-2-one. In the preparation of the latter compound (cf. A., 1915, i, 818), acetone sodium (Freer, A., 1894, i, 65) and 1-methyl*cyclo*hexan-2-ol are formed as by-products. 1-*Methyl*-3-*benzoxymethylene*cyclo*hexan*-2-*one* (needles, m. p. 84—85°) is hydrolysed more readily by acids than by alkalis.

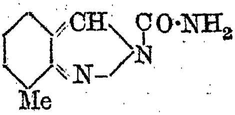
Semicarbazide reacts with hydroxymethylene*cyclo*hexanone to give tetrahydroindazole-2-carbonamide (Wallach and Steindorff, A., 1904, i, 104), the constitution of which is now definitely established by its formation by the hydrolysis of the *semicarbazone* of benzoxymethylene*cyclo*hexanone (needles, m. p. 193° if bath previously heated at 190°). Excess of semicarbazide converts the hydroxymethylene ketone into the *disemicarbazone* (I), which in hot dilute sulphuric acid solution affords the above carbonamide. The latter, as shown by Wallach (*loc. cit.*) occurs in two forms, although the latter author's m. p. observations are incorrect. The carbonamide, if obtained in the labile form (as in the first method given above), has m. p. 158°, but unless the m. p. bath is previously heated to within a few degrees of this temperature, the labile form passes, before its m. p. is reached, into the stable form (m. p. 186—188°) (see *infra*). Wallach's second m. p. (220°) actually indicated the decomposition of the carbonamide to give cyanuric acid.

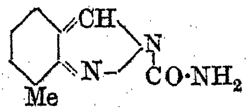


(I.)

The above disemicarbazone (I) had m. p. 193° when first prepared, but after six months, m. p. 203°. The lower m. p. is that of the labile form, which was not subsequently obtained. The substance becomes solid after melting at 203°, re-melting, with decomposition, at 234—236°.

Methyl-hydroxymethylene*cyclo*hexanone affords (with semicarbazide in cold acetic acid solution) the normal *semicarbazone* (white needles, m. p. 193° or 203°, according to the rate of heating), the *benzoyl* derivative of the latter being identical with the *semicarbazone* (m. p. 186°) of methyl-benzoxymethylene*cyclo*hexanone. Excess of semicarbazide converts the methyl hydroxymethylene ketone into the *disemicarbazone* (prisms, m. p. 215° if heated suddenly, and 237° [decomp.]), together with a little 7-*methyltetrahydroindazole*-2-*carbonamide*, the latter also being formed in small quantities in the preparation of the monosemicarbazone. The carbonamide exists in two forms: *labile* form, monoclinic needles, m. p. 138° (if plunged suddenly into bath just below 138°), then solidifying to give the *stable* form, tetragonal crystals, m. p. 163°. The labile form can be kept at the ordinary temperature, but passes into the stable form on heating in a toluene vapour-bath, or on boiling in alcoholic solution. The labile form results when the semicarbazone is treated in cold acetic acid solution with a little sulphuric acid, with subsequent addition of water, whereas if the solution is heated before addition of water, the latter precipitates the stable form. Again, when the parent ketone is treated with semicarbazide in presence of mineral acid, the carbonamide is formed, the production of the labile or of the stable form depending on the hydrogen-ion concentration. The carbonamide is converted by ammoniacal silver nitrate solution into the *silver* salt of 7-methyltetrahydroindazole, this salt, with carbamyl chloride, affording a mixture of the two forms of the carbonamide. The latter are shown to be stereoisomerides (see annexed formulæ), and not structural isomerides. They are readily interconvertible; moreover, under conditions when a 1-derivative might be expected to result (as when the parent ketone is treated with semicarbazide hydrochloride), the labile form, already proved to be a 2-derivative, is obtained. Polymorphism is also excluded as an explanation of the isomerism, on experimental grounds.





Tetrahydroindazole (m. p. 84°), first obtained by Wallach (*loc. cit.*), is prepared by boiling tetrahydroindazole-2-carbonamide (or the parent semicarbazones) with mineral acids, and gives the following derivatives: *picrate*, m. p. 155—156°; *silver* salt; 2-*acetyl* derivative, b. p. 130°/15 mm.; and 2-o-*nitrobenzoyl* derivative, white needles, m. p. 129—130°.

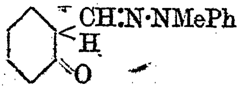
7-*Methyltetrahydroindazole* is a viscous oil, b. p. 152·8°/12 mm., becoming solid at the temperature of mixtures of ether and solid carbon dioxide. The following derivatives are described: *hydrochloride*, white prisms; *picrate*, m. p. 151—152°; *mercuric chloride additive* compound, white needles; *silver nitrate additive* compound, $Ag(C_8H_{12}N_2)_2NO_3$, white needles, m. p. 132°; *silver* salt, $C_8H_{11}N_2Ag$ (two forms, one soluble and one insoluble in ether); 2-*phenyl*-

carbonamide, white prisms, m. p. 70° (from the indazole and phenylcarbimide); and 2-o-*nitrobenzoyl* derivative, leaflets, m.p. 104—107°. The parent indazole is obtained either by treating methyl-hydroxymethylene*cyclo*hexanone semicarbazone with hot dilute sulphuric acid, or the ketone itself with hydrazine.

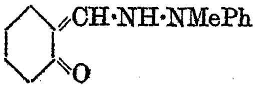
Hydroxymethylene*cyclo*hexanone, when treated with phenylhydrazine, gives a mixture of 1- and 2-phenyltetrahydroindazoles, which are not interconvertible and are separable as the picrates. The constitution of the 2-phenyl derivative follows from its formation from the benzoylated ketone and phenylhydrazine. The intermediately formed *phenylhydrazone* of the benzoylated ketone has only a transitory existence (white needles, m. p. about 80°), and rapidly passes into the above 2-phenylindazole derivative. 1-*Phenyl*-4 : 5 : 6 : 7-*tetrahydroindazole* forms leaflets, m. p. 58—59°, b. p. 178°/10 mm. (*picrate*, m. p. 125—126°, and *perchlorate* are described). 2-*Phenyltetrahydroindazole* forms prisms, m. p. 48·5—49·5°, b. p. 177°/10 mm. (*picrate*, m. p. 126·5—127·5°, and *perchlorate* are described).

In the interaction of hydroxymethylene*cyclo*hexanone and phenylhydrazine, the higher the concentration of hydrion, the smaller the proportion of 2-phenyl derivative formed, particularly if, at the same time, the temperature is kept low. Thus, when the ketone is treated at 0° with phenylhydrazine hydrochloride, only the 1-phenyl derivative is formed. This is explained as being due to the driving back, by hydrion, of the dissociation of the hydroxymethylene group, with resulting increase in the proportion of the aldehydic form, from which the 1-compound would be formed (cf. Claisen, A., 1895, i, 62). In this connexion, the nature of the hydrazine derivative affects the proportion of 1- to 2-derivative obtained, this being, under comparable conditions, as follows: phenylhydrazine, 1 : 0, *as*-phenylmethylhydrazine, 2 : 1, benzylhydrazine, 3 : 4, methylhydrazine, 4 : 1, and semicarbazide, 0 : 1.

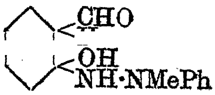
In order to throw light on the constitution of the intermediate compounds formed in the interaction of phenylhydrazine and hydroxymethylene*cyclo*hexanone, the interaction of the latter with phenylmethylhydrazine has been studied. The main product (m. p. 170—171°) is insoluble in alkali and may be either the *phenylmethylhydrazone* of 2-*keto*cyclo*hexylformaldehyde* (II) or 1-*methylphenylhydrazidomethene*cyclo*hexan*-2-*one* (III). A second product, soluble in alkali, is the *hydrate* (needles, m. p. 123—124°) of the *acid* produced by the spontaneous oxidation of IV. There is also formed a third product (under slightly different conditions), viz., the *hydrate* of the *phenylmethylhydrazone* of 1-*formyl*cyclo*hexan*-2-*one* (needles, m. p. 125—126°).



(II.)



(III.)



(IV.)

Methyl-hydroxymethylene*cyclo*hexanone, with phenylhydrazine, affords a mixture of the 1- and 2-indazole derivatives, low temperatures and high concentrations favouring the production of the 1-derivative. The latter is a stronger base than the 2-derivative, and forms a stable *perchlorate* (m. p. 214—215°), which allows of its separation from its isomeride. The benzoyl derivative of the methyl*cyclo*hexanone affords a *phenylhydrazone* (m. p. 125°, with previous sintering), which rapidly passes, in solution, into 2-*phenyl-7-methyl-*4 : 5 : 6 : 7-*tetrahydroindazole* (a colourless oil, b. p. 181·4°/10 mm. The *methiodide*, m. p. 172°, gives 2-phenyltetrahydroindazole when heated). 1-*Phenyl-*7-*methyltetrahydroindazole* is a colourless oil, b. p. 175°/10 mm.; its *methiodide*, m. p. 154°, on heating, gives 1-phenyltetrahydroindazole.

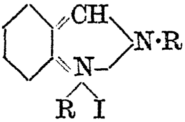
The products of the alkylation of tetrahydroindazole depend on the nature of the alkyl group introduced and on the experimental conditions. Tetrahydroindazole, when heated in alcoholic solution with benzyl chloride in presence of alkali, or when heated alone with the chloride at water-bath temperatures, affords a mixture of the 1- and 2-benzyl derivatives, this mixture also being obtained by condensing benzylhydrazine with hydroxymethylene*cyclo*hexanone. The benzoyl derivative of the latter ketone is converted by benzylhydrazine into 2-*benzylindazole* (colourless oil, b. p. 177°/10 mm.). 1-*Benzyltetrahydroindazole* is a colourless oil, b. p. 172°/10 mm. (*picrate*, m. p. 128—129°, and *perchlorate* are described).

Tetrahydroindazole, when heated at 100° with ethyl bromide, gives 2-*ethyltetrahydroindazole* (a colourless oil, b. p. 118°/15 mm.; *picrate* has m. p. 150·5—151·5°), whilst when similarly heated in presence of alkali, it affords 1-*ethyltetrahydroindazole* (a colourless oil, b. p. 111°/14 mm.; *picrate* has m. p. 103—104°).

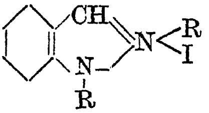
The methylation of tetrahydroindazole leads, in presence or in absence of alkali, to the formation of the 1- and 2-methyl derivatives, which cannot be separated. 2-*Methyltetrahydroindazole*, obtained from benzoxymethylene*cyclo*hexanone, is a colourless oil, b. p. 93—94°/9 mm. or 103°/13 mm. (*picrate*, m. p. 166·5—167·5°).

7-Methyltetrahydroindazole on methylation, ethylation, or benzylation, in presence or in absence of alkali, always affords 2-derivatives, which may be obtained from the appropriate hydrazine and methylbenzoxymethylene*cyclo*hexanone. 2 : 7-*Dimethyl-*4 : 5 : 6 : 7-*tetrahydroindazole* is a colourless oil with a feeble blue fluorescence, has b. p. 111°/13 mm., and forms a *picrate*, m. p. 123—125°. 7-*Methyl-2-ethyltetrahydroindazole*, a colourless oil, b. p. 108·5°/10 mm., gives a *picrate*, m. p. 101—102°, and a *methiodide*, m. p. 102—103°, the latter affording 7-methyl-2-ethyltetrahydroindazole when heated. 7-*Methyl-*2-*benzyltetrahydroindazole*, a colourless oil, b. p. 181—183°/12 mm. or 152°/3 mm., forms a *methiodide* (leaflets, m. p. 175° [decomp.]), which is also obtained from 2 : 7-dimethyltetrahydroindazole and benzyl iodide, and, on heating, affords the two last-named substances. The fact that the 7-methyl group prevents alkylation in position 1 is to be ascribed to electrochemical (not stereochemical) effects (cf. attempts to prepare 1 : 5-dialkylpyrazoles by Auwers and Broche, A., 1923, i, 151).

The formation of quaternary salts from the reduced indazoles is not altogether parallel to their formation in the ordinary series. The 2-methyl- and 2-ethyl-tetrahydroindazoles follow the general rule. Methyl iodide converts either 1- or 2-methyltetrahydroindazole into 1 : 2-*dimethyl*-4 : 5 : 6 : 7-*tetrahydroindazolium iodide* (m. p. 152—153°). Ethyl iodide converts either 1- or 2-ethyltetrahydroindazole into 1 : 2-*diethyltetrahydroindazolium iodide* (m. p. 98—99°). Since these quaternary salts afford mixtures of 1- and 2-alkyl derivatives when heated, they are given formulæ V or VI, or, better, VII :



(V.)



(VI.)

$[C_6H_8{\cdot}CH(N^2R)(N^1R)]I.$

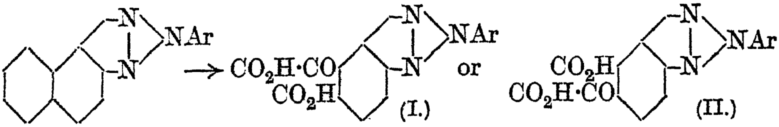
(VII.)

2-Benzyltetrahydroindazole, when heated with ethyl iodide, affords the *compound* (m. p. 138—139°) obtained by heating 2-ethyltetrahydroindazole with benzyl iodide. The compound, on heating, affords pure 2-ethyltetrahydroindazole, and therefore is written as $[C_6H_8{\cdot}CH(N^2Et[Ph{\cdot}CH_2{\cdot}])(N^1)]I$, both alkyl groups being attached to the same nitrogen atom. Similarly, the *compound*, $[C_6H_8{\cdot}CH(N^2)(N^1Et[Ph{\cdot}CH_2{\cdot}])]I$ (m. p. 127—128°), is formed from 1-benzyltetrahydroindazole and ethyl iodide or from the 1-ethyl derivative and benzyl iodide. The 1 : 1-quaternary salt, on heating, affords, not 1-ethyl-, but 2-ethyl-tetrahydroindazole.

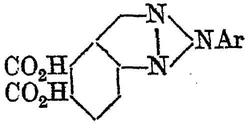
7-Methyltetrahydroindazole gives quaternary salts in which the two alkyl groups are attached to the same nitrogen atom (see *ante*). The *methiodides* of 1- and 2-phenyltetrahydroindazoles afford, when heated, the parent phenyl derivatives.

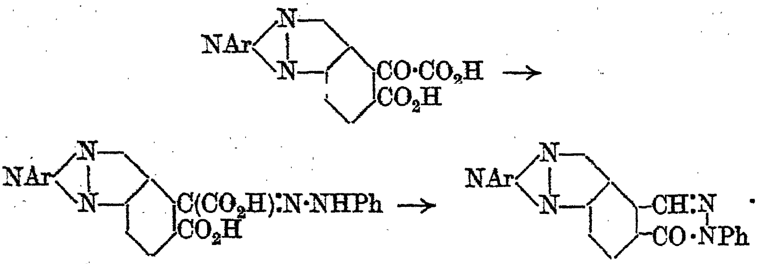
7-Methyltetrahydroindazole reacts with ethyl bromoacetate to give *ethyl* 7-*methyl*-4 : 5 : 6 : 7-*tetrahydroindazyl*-2-*acetate* (colourless oil, b. p. 166·5—167·5°/14 mm.; *picrate*, m. p. 127—130° [indef.]). The corresponding *acid* (also obtainable from the indazole and chloroacetic acid), obtained by hydrolysis, forms white needles, m. p. 168—169° (*silver* salt described), and has, unlike the indazole bases, a sweet taste. E. E. T.

***vic.*-2 : *N*-Aryltriazolephthalonic Acids.** G. CHARRIER (*Gazzetta*, 1923, **53**, 829—843).—It has been shown by Dimroth (A., 1902, i, 403) that, starting from the three isomeric *N*-phenyl derivatives of 1 : 2 : 3-triazolemonocarboxylic acid and eliminating the phenyl group by oxidation after nitrating and converting into the amino-derivative by reduction, one and the same acid is obtained; the desmotropy of the triazole ring is thus established. Oxidation of naphthalene by means of alkaline permanganate solution yields mainly phthalonic acid, and the author finds similarly that the 2-arylnaphthatriazoles give, under the same conditions, principally the corresponding vicinal 2-aryltriazolephthalonic acids,



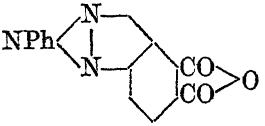
Since these acids are highly stable towards oxidising agents and are prone to form monometallic salts with the alkali metals, probably owing to the formation of an internal anhydride between the $\cdot CO\cdot CO_2H$ group and the triazole ring, and further on account of the analogy existing between them and the product of the oxidation of naphthalic acid by permanganate in alkaline solution (cf. Graebe and Bossel, A., 1893, i, 593), formula (I) is regarded as preferable to formula (II). The constitution of these acids is shown also by their oxidation to the corresponding 2-aryltriazolephthalic acids (annexed formula), and by their ability to react as keto-acids, analogously to phthalonic acid, with phenylhydrazine hydrochloride to form phenylhydrazones. The latter are far more stable than those of phthalonic acid, since only by heating above their melting points are they transformed, like phenylhydrazones of a keto-acid, into derivatives of the corresponding ketotetrahydropyridazines (pyridazinones); a carboxyl group is eliminated at the same time, so that from a dibasic acid a neutral heterocyclic derivative is obtained:

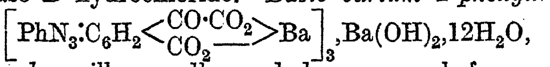




These acids behave as comparatively strong dibasic acids; they decompose carbonates, form well crystallised salts containing water of crystallisation, and readily yield normal and acid esters and amides. When subjected to prolonged energetic oxidation, they give the corresponding phthalic acids.

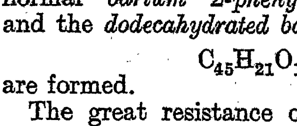
[With A. Odifreddi, A. Manfredi, and E. Mars.]—vic.-2-*Phenyltriazolephthalonic acid*, $C_{15}H_9O_5N_3$, obtained by oxidising 2-phenylnaphthatriazole, crystallises in white or lustrous needles, m. p. 242°, and has an intense acid reaction towards litmus, methyl orange and phenolphthalein. It yields the following derivatives: *monosodium* salt, $C_{15}H_8O_5N_3Na,4H_2O$, m. p. 324—325°, gives aqueous solutions acid to litmus and phenolphthalein. The normal



barium salt crystallises with $4H_2O$ and also with $5H_2O$, and when subjected to dry distillation in the anhydrous state yields vic.-2-*phenyltriazolephthalic anhydride* (annexed formula), which crystallises in slender, white needles, m. p. 183—184°, and, when treated with *m*-diethylaminophenol and zinc chloride, gives a deep red, crystalline colouring matter; the hydrochloride of the latter dissolves in boiling alcohol to an intense reddish-violet, markedly fluorescent solution, and crystallises in slender, metallic green needles similar to the crystals of rhodamine base B hydrochloride. *Basic barium 2-phenyltriazolephthalonate,*  $\left[PhN_3{:}C_6H_2<{}^{CO\cdot CO_2}_{CO_2}>Ba\right]_3,Ba(OH)_2,12H_2O$, forms rosettes of slender, silky needles and decomposes before melting. The *strontium* salt, $C_{15}H_{17}O_5N_3Sr,4\frac{1}{2}H_2O$, forms lustrous, white needles and decomposes before melting. The *methyl* ester, $C_{13}H_7ON_3(CO_2Me)_2$, forms minute, white prisms, m. p. 87—88°, and the *methyl hydrogen* ester, $C_{16}H_{11}O_5N_3$, colourless, prismatic crystals, m. p. 201—202°. The *ethyl* ester crystallises in colourless prisms, m. p. 169—170°. The *diamide*, $C_{13}H_7ON_3(CO\cdot NH_2)_2$, forms lustrous, colourless prisms, m. p. 233—234°, and, when boiled with 10% ammonia solution, yields the *ammonium* salt of the *monoamide*, $C_{15}H_{13}O_4N_5$, which crystallises in slender, white needles, m. p. 250° (decomp.). The *phenylhydrazone*, probably

$$Ph\cdot N_3{:}C_6H_2(CO_2H)\cdot C(CO_2H){:}N\cdot NHPh,$$

crystallises in white, silky needles, m. p. 206—207° (decomp.), and acts as an energetic acid.



The monocarboxylic ketotetrahydropyridazinic acid, that is, the pyridazinone of *vic.*-2-phenyltriazolephthalonic acid, is not formed when the phenylhydrazone is boiled in acetic acid, but when heated at 250° the phenylhydrazone loses carbon dioxide and water, to give the decarboxylated *pyridazinone* (annexed formula), which crystallises in colourless prisms, m. p. about 200°. When the phenylhydrazone is treated in boiling water with barium carbonate, phenylhydrazine separates and the pentahydrated normal *barium 2-phenyltriazolephthalonate*, $C_{15}H_7O_5N_3Ba,5H_2O$, and the *dodecahydrated basic barium* salt,

$$C_{45}H_{21}O_{15}N_9Ba_3,Ba(OH)_2,12H_2O,$$

are formed.

The great resistance offered by *vic.*-2-phenyltriazolephthalonic acid to oxidising agents may be due to the existence of an anhydridic linking between the triazole nucleus and the $\cdot CO\cdot CO_2H$ group, which is thus protected from the action of nascent oxygen. The acid is, however, attacked by chromic acid with formation of a *compound* which crystallises in aggregates of radiating leaflets, m. p. 250°, acts as an energetic acid, and has the nitrogen content of a *vic.*-2-phenyltriazolephthalic acid.

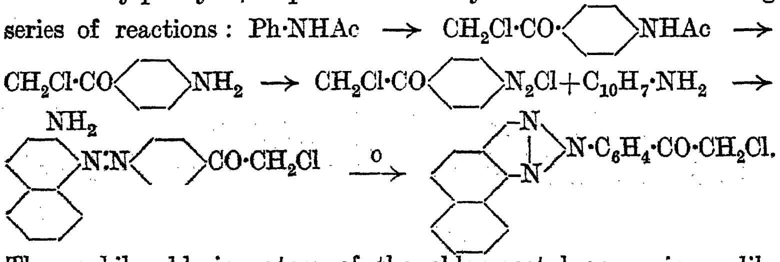
vic.-2-p-*Chlorophenyltriazolephthalonic acid*,
$C_6H_4Cl\cdot N_3\colon C_6H_2(CO_2H)\cdot CO\cdot CO_2H$,
crystallises in slender, white needles, m. p. 264—265°; its *monosodium* salt ($+2H_2O$) does not melt at 360°.

2-p-*Bromophenylnaphthatriazole*, $C_{10}H_6\cdot N_3\cdot C_6H_4Br$, prepared by oxidising *p*-bromophenylazo-β-naphthylamine by means of chromic acid in acetic acid solution, crystallises in white, silky needles, m. p. 200°.

vic.-2-p-*Bromophenyltriazolephthalonic acid*, obtained by the action of alkaline permanganate solution on the preceding compound, forms flat, white needles, m. p. 270°; its *monosodium* salt ($+2H_2O$) does not melt at 320°.

vic.-2-p-*Carboxyphenyltriazolephthalonic acid*, $C_{16}H_9O_7N_3$, crystallises in slender, white needles, m. p. 287—288° (decomp.), and is an energetic tribasic acid; its *monosodium* salt ($+4\frac{1}{2}H_2O$) does not melt at 350°.
T. H. P.

αβ-Naphthatriazoles. G. Charrier and M. Gallotti (*Gazzetta*, 1923, **53**, 851—861).—The authors have prepared 2-*p*-chloroacetylphenyl-αβ-naphthatriazole by means of the following series of reactions :



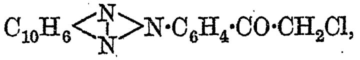
The mobile chlorine atom of the chloroacetyl group is readily replaced, giving the corresponding iodo- and cyano-derivatives. Hydrolysis of the latter gives the unstable ketonic acid, which loses carbon dioxide to form the corresponding ketone, 2-*p*-acetylphenyl-αβ-naphthatriazole. Treatment of the chloroacetyl compound with silver acetate yields the acetyl derivative of the corresponding ketocarbinol, αβ-naphthatriazole-2-*p*-benzoylcarbinol, which may be obtained either by hydrolysis of the acetyl derivative or by the action of moist silver oxide on the chloroacetyl compound itself. The latter reacts normally with ammonia, yielding αβ-naphthatriazole-2-*p*-benzoylmethylamine, whilst with primary aliphatic amines both substitution and addition occur, the unstable compound thus formed losing water and alkylamine when treated with an acid or even with a solvent :

$$C_{10}H_6\colon N_3\cdot C_6H_4\cdot CO\cdot CH_2Cl \longrightarrow C_{10}H_6\colon N_3\cdot C_6H_4\cdot CO\cdot CH_2\cdot NHR,xNH_2R$$
$$\longrightarrow C_{10}H_6\colon N_3\cdot C_6H_4\cdot C(\colon NR)\cdot CH_2\cdot NHR;$$

the resulting compound consists of the corresponding 2-*p*-β-alkylamino-α-alkyliminoethylphenyl-αβ-naphthatriazole. Aniline acts similarly to ammonia, the chlorine atom of the *p*-chloroacetyl group being replaced by the anilino residue.

[With R. SALA, Q. MINGOIA, and P. TORAZZI.]—p-*Chloroacetylbenzeneazo-β-naphthylamine*, $NH_2\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot CO\cdot CH_2Cl$, crystallises in thin, lustrous, garnet-red leaflets, m. p. 172°, and dissolves in concentrated sulphuric acid to a magenta-red solution. Its *phenylhydrazone* forms a red, crystalline powder with metallic green reflex, m. p. 180° (decomp.).

2-p-*Chloroacetylphenyl-αβ-naphthatriazole*,



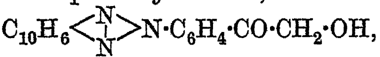
$$C_{10}H_6<\overset{N}{\underset{N}{|}}>N\cdot C_6H_4\cdot CO\cdot CH_2Cl,$$

prepared by oxidising the preceding compound by means of chromic acid, forms thin, white leaflets, m. p. 198°, and dissolves in concentrated sulphuric acid to a yellow solution. Its *phenylhydrazone* crystallises in thin, pale yellow leaflets, m. p. 156°.

2-p-*Iodoacetylphenyl-αβ-naphthatriazole* separates in lustrous, white needles, m. p. 195°.

2-p-*Cyanoacetylphenyl-αβ-naphthatriazole*, $C_{19}H_{12}ON_4$, crystallises in slender, yellow needles, m. p. 185°, with previous contraction, and, on protracted boiling with 50% sulphuric acid, gives 2-*p*-acetylphenyl-αβ-naphthatriazole (cf. A., 1922, i, 771).

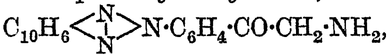
αβ-*Naphthatriazole*-2-p-*benzoylcarbinol*,



$$C_{10}H_6<\overset{N}{\underset{N}{|}}>N\cdot C_6H_4\cdot CO\cdot CH_2\cdot OH,$$

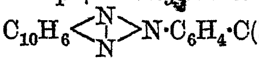
crystallises in silvery leaves, m. p. 191°, and its *acetyl* derivative in slender, white needles, m. p. 187°.

αβ-*Naphthatriazole*-2-p-*benzoylmethylamine*,



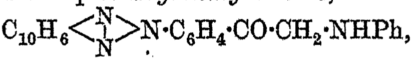
$$C_{10}H_6<\overset{N}{\underset{N}{|}}>N\cdot C_6H_4\cdot CO\cdot CH_2\cdot NH_2,$$

forms minute, almost colourless crystals, m. p. 192°, and gives a pale yellow *hydrochloride*, m. p. 184°.

2-p-β-*Methylamino-α-methyliminoethylphenyl-αβ-naphthatriazole*,  $C_{10}H_6<\overset{N}{\underset{N}{|}}>N\cdot C_6H_4\cdot C({:}NMe)\cdot CH_2\cdot NHMe$, crystallises in yellow needles, m. p. 160°, and forms a yellowish-brown hydrochloride.

2-p-β-*Ethylamino-α-ethyliminoethylphenyl-αβ-naphthatriazole*, $C_{22}H_{23}N_5$, separates in slender, pale yellow needles, m. p. about 150° with previous contraction.

αβ-*Naphthatriazole*-2-p-*benzoylmethylaniline*,

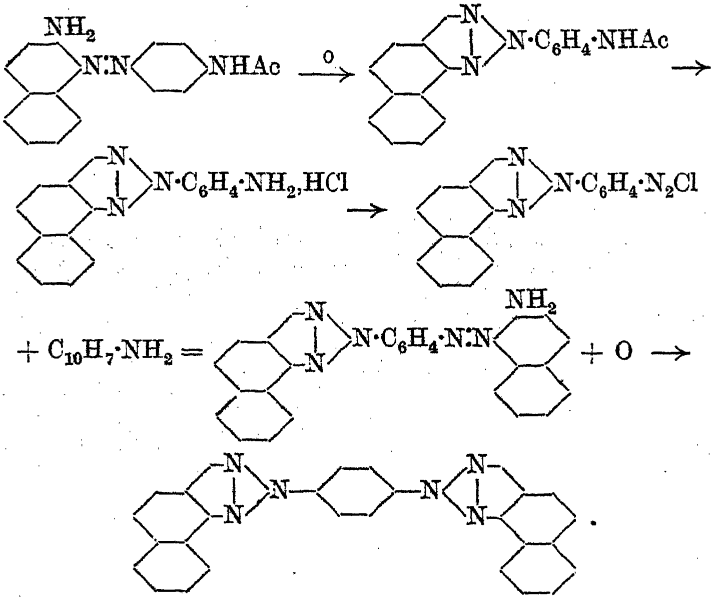


$$C_{10}H_6<\overset{N}{\underset{N}{|}}>N\cdot C_6H_4\cdot CO\cdot CH_2\cdot NHPh,$$

crystallises in lustrous, sulphur-yellow leaflets, m. p. 277°, and forms benzene solutions exhibiting pronounced greenish-yellow fluorescence; its *phenylhydrazone* separates in slender, lemon-yellow needles, m. p. about 270° (decomp.). T. H. P.

Oxidation of Uric Acid by Iodine in Alkaline Solution. J. MORE (*Compt. rend.*, 1924, **178**, 498—501).—Oxidation of uric acid (1 mol.) by iodine (2 atoms), in potassium hydrogen carbonate solution, affords a substance (not isolated), which is converted by acetic acid into allantoin, and (cf. Biltz and Max, A., 1921, i, 893) is further oxidisable by iodine in acid solution. Oxidation of uric acid by means of iodine in sodium hydroxide solution (cf. Kreidl, A., 1893, ii, 558) gives first a substance which affords a uroxanate on evaporation in alkaline solution, or allantoin on evaporating in acetic acid solution, and in presence of alkali may also pass into a less readily oxidised isomeride. The latter, however, yields the same products as above, on evaporation in alkaline or acid solution, and on oxidation with iodine gives *allantoxalic amide*. The latter, when treated with concentrated potassium hydroxide, affords potassium allantoxalate; the following *salts* are described: $C_4H_3O_3N_4K,1{\cdot}5H_2O$; $C_4H_3O_3N_4Na,1{\cdot}5H_2O$, and $C_4H_3O_3N_4(NH_4),H_2O$. E. E. T.

p-Phenylene-1:2-dinaphthaditriazole. G. CHARRIER (*Gazzetta*, 1923, **53**, 862—867).—This compound has been prepared by means of the following series of reactions: $C_6H_5{\cdot}NHAc \longrightarrow NO_2{\cdot}C_6H_4{\cdot}NHAc \longrightarrow NH_2{\cdot}C_6H_4{\cdot}NHAc \longrightarrow N_2Cl{\cdot}C_6H_4{\cdot}NHAc + C_{10}H_7{\cdot}NH_2 \longrightarrow$



It is a highly stable compound and, as is usual with αβ-naphthatriazoles, is oxidised by permanganate in alkaline solution, giving *vic.-p*-phenyleneditriazolediphthalonic acid. Derivatives of the *p*-phenylene-1:2-dinaphthaditriazole have not previously been prepared (cf. Morgan and Chazan, A., 1922, i, 181). It is found possible to pass directly, by oxidation by means of alkaline permanganate solution, from 1:2-naphthatriazole-2-*p*-benzeneazo-β-naphthylamine to the above diphthalonic acid, preparation of the corresponding naphthatriazole as an intermediate product being unnecessary. Similarly, *vic.*-2-phenyltriazolephthalonic acid may be prepared directly from 1-benzeneazo-2-naphthylamine.

[With G. BONOMI and T. BETTINAZZI.]—*p*-Acetylaminobenzeneazo-β-naphthylamine, $C_{18}H_{16}ON_4$, prepared by the interaction of *p*-acetylaminophenyldiazonium chloride and β-naphthylamine in alcoholic solution, crystallises in slender, orange-red needles, m. p. 208°.

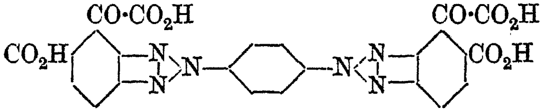
2-p-*Acetylaminophenyl*-1 : 2-*naphthatriazole*, $C_{18}H_{14}ON_4$, obtained by oxidising the preceding compound in acetic acid solution by means of chromic acid, forms slender, white needles, m. p. 228°, and exhibits marked blue fluorescence even in very dilute solutions.

2-p-*Aminophenyl*-1 : 2-*naphthatriazole*, $C_{16}H_{12}N_4$, crystallises in lustrous, silky, white needles, m. p. 200°.

1 : 2-*Naphthatriazole*-p-*benzeneazo*-β-*naphthylamine*, $C_{26}H_{18}N_6$, separates in bright red needles, m. p. 250°.

p-*Phenylene*-1 : 2-*dinaphthaditriazole*, $C_{26}H_{16}N_6$, forms thin, pink laminæ, m. p. 333°.

vic.-p-*Phenyleneditriazolediphthalonic acid* (annexed formula), crystallises in slender, white needles, m. p. 322—323°, with slight browning at 320°.



2-*Phenyltriazolephthalonic acid*, $Ph\cdot N_3{:}C_6H_2(CO_2H)\cdot CO\cdot CO_2H$ [$N_3Ph : CO_2H : CO\cdot CO_2H = 12 : 4 : 3$], prepared by oxidising benzeneazo-β-naphthylamine by means of alkaline permanganate solution, crystallises in lustrous, white needles, m. p. 242°. T. H. P.

s-Trinitroarylazodiarylamines. A. BERETTA (*Gazzetta*, 1923, **53**, 870—876).—By the action of picryl chloride on aminoazo-derivatives in alcoholic solution in presence of sodium acetate, the author has prepared the *s*-trinitrophenyl derivatives of various *o*-, *m*-, and *p*-aminoazo-compounds of the benzene and naphthalene series.

3′-*Benzeneazo*-2 : 4 : 6-*trinitrodiphenylamine*,

$$(NO_2)_3C_6H_2\cdot NH\cdot C_6H_4\cdot N{:}NPh,$$

obtained from *m*-aminoazobenzene, crystallises in slender, yellow needles, m. p. 212°, and dissolves in concentrated sulphuric acid to a yellow solution. 4′-Benzeneazo-2 : 4 : 6-trinitrodiphenylamine (cf. Walther and Lehmann, A., 1904, i, 352) has m. p. 178°. 3′-*Methyl*-6′-p-*tolueneazo*-2 : 4 : 6-*trinitrodiphenylamine*,

$$C_6H_4Me\cdot N{:}N\cdot C_6H_3Me\cdot NH\cdot C_6H_2(NO_2)_3,$$

prepared from *p*-tolueneazo-*p*-toluidine, forms slender, slightly orange, red crystals, m. p. 201°, and gives a red solution in concentrated sulphuric acid. 2′-*Methyl*-4′-o-*tolueneazo*-2 : 4 : 6-*trinitrodiphenylamine* crystallises in red needles, m. p. 194°, and dissolves in concentrated sulphuric acid to a red solution. 3′-*Amino*-4′-*benzeneazo*-2 : 4 : 6-*trinitrodiphenylamine*, $C_{18}H_{13}O_6N_7$, prepared from 2 : 4-diaminoazobenzene (chrysoidine), forms minute, red crystals, m. p. 254° (decomp.), and gives a red solution in concentrated sulphuric acid. 3′-*Amino*-6′-*methyl*-4′-*benzeneazo*-

2 : 4 : 6-*trinitrodiphenylamine*, $C_{19}H_{15}O_6N_7$, prepared from 2 : 4-diaminoazomethylbenzene (methylchrysoidine), forms slender, lustrous prisms with metallic reflexion, m. p. 228° (decomp.), and dissolves in concentrated sulphuric acid to a red solution. 3′-*Acetylamino*-6′-*methyl*-4′-*benzeneazo*-2 : 4 : 6-*trinitrodiphenylamine* crystallises in slender, orange-yellow prisms, m. p. 215° (decomp.). 3′-*Amino*-6′-*methyl*-4′-p-*chlorobenzeneazo*-2 : 4 : 6-*trinitrodiphenylamine*, $C_{19}H_{14}O_6N_7Cl$, prepared from 4′-chloro-2 : 4-diamino-5-methylazobenzene, crystallises in slender, metallic brown prisms, m. p. 235° (decomp.), and forms a red solution in concentrated sulphuric acid. The corresponding 3′-*acetylamino*-compound separates in slender, orange crystals, m. p. 228° (decomp.). 3′-*Amino*-6′-*methyl*-4′-p-*bromobenzeneazo*-2 : 4 : 6-*trinitrodiphenylamine*,

$$C_{19}H_{14}O_6N_7Br,$$

crystallises in slender, lustrous, brown needles, m. p. 233° (decomp.), and dissolves in concentrated sulphuric acid to a red solution. The corresponding *acetylamino*-derivative forms slender, orange needles, m. p. 227° (decomp.).

α-*Benzeneazo*-β-*naphthyl*-2 : 4 : 6-*trinitrophenylamine*,

$$Ph{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH{\cdot}C_6H_2(NO_2)_3,$$

prepared from benzeneazo-β-naphthylamine, crystallises in slender, reddish-brown needles, m. p. 221° (decomp.), and dissolves in concentrated sulphuric acid to a blue solution. α_2-*Benzeneazo*-α_1-*naphthyl*-2 : 4 : 6-*trinitrophenylamine* forms slender, reddish-brown needles, m. p. 193° (decomp.), and yields a blue solution in concentrated sulphuric acid. T. H. P.

Studies in Dyes with Multiple Chromophores. R. N. SEN and B. SETT (*J. Amer. Chem. Soc.*, 1924, **46**, 111—119).—Three types of azo-triphenylmethane dyes have been studied containing, respectively, one, two, and three azo-groups in the *p*-position to the central carbon atom. It has been found that the introduction of one azo-group deepens the colour (compare T., 1912, **101**, 1113), of two azo-groups lightens the colour, and of three makes it still lighter. The effect of the multiplication of chromophores has also been studied by introducing simultaneously an azo-methine group and an azo-group into chrysoidine, rosaniline, safranine, and Congo-red, and in each case the colour becomes lighter. The direct-dyeing property of Congo-red also disappears. The introduction of the azo-group has been found to deepen the colour in the case of an indamine dye as well as in the case of fluorescein.

The preparation and properties of the following dyes, which appear to be new substances, are described: *phenetoleazosulphophenyltetramethyldiaminodiphenylcarbinol* (from phenetoleazobenzaldehydesulphonic acid and dimethylaniline) dyes wool green; *dimethylaminobenzeneazophenyltetramethyldiaminodiphenylcarbinol* (from benzeneazodimethylaniline and tetramethyldiaminobenzhydrol) dyes wool blue; *salicylylazophenyldisalicylylcarbinol* (from methylenedisalicylic acid and benzeneazosalicylic acid) dyes wool red; *phenyldi(dimethylaminobenzeneazophenyl)carbinol* (from benzaldehyde and benzeneazodimethylaniline) dyes wool violet; *phenetoleazosulphophenyldi(dimethylaminobenzeneazophenyl)carbinol* (from phenetoleazobenzaldehydesulphonic acid and benzeneazodimethylaniline) dyes wool yellow; *diphenetoleazosulphobenzylidenechrysoidine* (from chrysoidine hydrochloride and phenetoleazobenzaldehydesulphonic acid) dyes wool golden-yellow; *diphenetoleazosulphobenzylidene-rosaniline hydrochloride* (from rosaniline and phenetoleazobenzaldehydesulphonic acid) dyes wool bluish-red; *diphenetoleazosulphobenzylidene-safranine hydrochloride* (from safranine and phenetoleazobenzaldehydesulphonic acid) dyes wool red; *dimethylaminobenzeneazophenyldimethylquinoneimine hydrochloride* (from nitrosodimethylaniline hydrochloride and benzeneazodimethylaniline) dyes wool olive-green; *sulphobenzeneazofluorescein* (from diazotised sulphanilic acid and fluorescein) dyes wool orange.

F. A. M.

Amine Oxidation. VIII. Oxidation of Aliphatic Amines. S. Goldschmidt and V. Voeth (*Annalen*, 1924, **435**, 265—277).—Benzylamine is oxidised by potassium permanganate in aqueous or in acetone solution to give benzaldehyde, no intermediate compound being isolable even if oxidation be effected at −60°. Since, however, benzaldehyde, under similar conditions, is rapidly oxidised to benzoic acid, it cannot be the primary product in the oxidation of benzylamine, which probably proceeds thus: $\mathrm{PhCH_2{\cdot}NH_2} \longrightarrow \mathrm{PhCH_2{\cdot}N{:}} \longrightarrow \mathrm{PhCH{:}NH} \longrightarrow \mathrm{PhCH{:}O+NH_3}$.

Dibenzylamine is oxidised by permanganate in acetone solution to give *benzoyltribenzylhydrazine* (white needles, m. p. 181°), the constitution of which was established by synthesis (from tribenzoylhydrazine and benzoyl bromide); its formation is explained by the scheme: $\mathrm{2(PhCH_2)_2NH} \longrightarrow \mathrm{2(PhCH_2)_2N{:}} \longrightarrow \mathrm{(PhCH_2)_2N{\cdot}N(CH_2Ph)_2} \longrightarrow \mathrm{(PhCH_2)_2N{\cdot}NBz{\cdot}CH_2Ph}$. Confirmation of this explanation was obtained: tetrabenzylhydrazine on oxidation with permanganate gives benzoyltribenzylhydrazine, which, on reduction with zinc dust and acetic acid, yields benzylbenzamide (and traces of benzaldehyde and dibenzylamine), and on treatment with mineral acids gives (per mol.) benzaldehyde (1 mol.) and *hydroxytribenzylhydrazine hydrochloride*. The latter (m. p. 220—240° [indef.]) could not be obtained in a pure state and was found to contain dibenzylamine hydrochloride, whilst, on treating it with alkali, benzamide and tribenzylhydrazine were isolated.

The oxidation of di-*n*-propylamine by means of permanganate gives *αβ-dipropionyl-αβ-di-*n*-propylhydrazine*,

$$\mathrm{COEt{\cdot}NPr^{\alpha}{\cdot}NPr^{\alpha}{\cdot}COEt}.$$

This substance, evidently formed by the oxidation of the first-formed tetrapropylhydrazine, was only obtained in a slightly impure state as a yellow oil possessing an odour like that of menthol, and beginning to decompose at 40° (more readily in presence of alkali) with formation of propaldehyde. The dipropionyl derivative, on being distilled, affords a mixture of propaldehyde, n-*propylpropionamide*, $\mathrm{NHPr^{\alpha}{\cdot}COEt}$ (pale yellow oil, b. p. 64—65°/

0·4 mm.), and n-*propylidenepropionamide*, CHEt:N·COEt (viscous, greenish-yellow oil, b. p. 87°/0·4 mm.).

Aqueous permanganate with piperidine gave no isolable products, but in acetone solution oxidation proceeded much more rapidly than in the cases described already, to give N-*piperidyl*-N-2-*piperidone* as a yellowish-red oil, which, on distillation, was converted into a mixture of tetrahydropyridine and 2-piperidone (b. p. 64—65°/0·4 mm.). E. E. T.

Certain Nitroarylhydrazines. M. Giua (*Gazzetta*, 1923, **53**, 844—851).—The results obtained when various aromatic nitro-compounds are treated with semicarbazide show that the latter serves to replace by the residue $\cdot NH\cdot NH\cdot CO\cdot NH_2$, not only the nitro-group, but also labile halogen atoms. Thus, when heated on a water-bath in alcoholic solution containing sodium acetate, 1-chloro-2 : 4-dinitrobenzene and semicarbazide react in accordance with the equation: $C_6H_3Cl(NO_2)_2+2NH_2\cdot NH\cdot CO\cdot NH_2=C_6H_3(NO_2)_2\cdot NH\cdot NH\cdot CO\cdot NH_2+NH_2\cdot CO\cdot NH\cdot NH_2,HCl$. In the case of nitro-compounds containing a labile nitro-group, the formation of nitrous acid renders the reaction somewhat complicated, and, although the yields of nitrophenylsemicarbazides are good, various secondary products are also formed. With β- and γ-trinitrotoluenes the first phase of the reaction is probably expressed by the equation: $C_6H_2Me(NO_2)_3+2NH_2\cdot NH\cdot CO\cdot NH_2=C_6H_2Me(NO_2)_2\cdot NH\cdot NH\cdot CO\cdot NH_2+NH_2\cdot CO\cdot N_3+2H_2O$; the azide of carbamic acid has not been observed among the secondary products, but small proportions of cyanuric acid, which is one of the many transformation products of this azide, have been detected (cf. Curtius and Schmidt, A., 1923, i, 1080).

4 : 6-*Dinitro*-m-*tolylsemicarbazide*, obtained by the action of semicarbazide on γ-trinitrotoluene, forms crystals, m. p. 237—238° (decomp.). 2 : 4-*Dinitro*-m-*tolylsemicarbazide*, similarly obtained from β-trinitrotoluene, forms crystals, m. p. 185° (decomp.), and in alcoholic solution yields a reddish-brown coloration with alkalis. 5-*Chloro*-2 : 4-*dinitrophenylsemicarbazide*, prepared from 1-chloro-2 : 4 : 5-trinitrobenzene, forms yellow crystals, m. p. 217—218° (decomp.). 2 : 4-*Dinitrophenylsemicarbazide*, $C_7H_7O_5N_5$, prepared from 1-chloro-2 : 4-dinitrobenzene, forms pale yellow crystals, m. p. 205—207° (decomp.).

α-*Methyl*-α-*phenyl*-5-*chloro*-2 : 4-*dinitrophenylhydrazine*,

$$Cl(NO_2)_2C_6H_2\cdot NH\cdot NMePh,$$

obtained by the interaction of *as*-methylphenylhydrazine and 1-chloro-3 : 4 : 6-trinitrobenzene, crystallises in orange-yellow lamellæ, m. p. 120—121°, and dissolves in concentrated sulphuric acid to a reddish-brown solution.

Acetone 4 : 6-*dinitro*-m-*tolylhydrazone*, $C_{10}H_{12}O_4N_4$, crystallises in yellow needles, m. p. 144—145°, and in alcoholic solution gives a dark red coloration with an alkali. Other 4 : 6-dinitro-*m*-tolylhydrazones are those of: *acetophenone*, $C_{15}H_{14}O_4N_4$, crystallising in orange-yellow needles, m. p. 215—216°; *ethyl phenyl ketone*, $C_{16}H_{16}O_4N_4$, forming a red, crystalline powder, m. p. 183—184°;

benzaldehyde, $C_{14}H_{12}O_4N_4$, crystallising in reddish-yellow needles, m. p. 224—225°; *anisaldehyde*, separating in garnet-red prisms, m. p. 238—239° (decomp.); p-*tolualdehyde*, $C_{15}H_{14}O_4N_4$, forming lustrous, deep red needles, m. p. 237—238°; *cinnamaldehyde*, $C_{16}H_{14}O_4N_4$, forming bright red needles, m. p. 263—264° (decomp.).

T. H. P.

Additive Reactions of the Phosphorus Halides. VIII. Kinetic Evidence in Regard to the Mechanism of the Reaction. J. B. Conant and V. H. Wallingford (*J. Amer. Chem. Soc.*, 1924, **46**, 192—202; cf. A., 1923, i, 498).—The reaction between benzaldehyde and phosphorus trichloride proceeds to a definite equilibrium both in the absence of a solvent and in benzene solution. The composition of the equilibrium mixture accords with the law of mass action. An earlier explanation of the mechanism of the reaction between carbonyl compounds, phosphorus trichloride, and acetic acid or anhydride assumed that this addition reaction was an intermediate step; this explanation is now abandoned. The gradual addition of small amounts of water to a mixture of benzaldehyde and the trichloride causes an irreversible reaction to take place. The product appears to be an open-chain phosphorus compound which readily loses hydrogen chloride to form a phostonic acid derivative (cf. Conant and Macdonald, A., 1921, i, 69). The reaction between a trichloride, an aldehyde, and acetic acid must be either a direct interaction of three molecules or a reaction in which some open-chain additive product of an unstable nature is an intermediate; the authors favour the latter alternative. F. A. M.

Action of Halogen Derivatives of Phosphorus on some Phenolic Bases. M. Bourneuf (*Bull. Soc. chim.*, 1923, **33**, [iv], 1808—1823).—When dimethylaniline (2 mols.) is heated at 70° with phosphorus trichloride (1 mol.), *p*-dimethylaminophenyldichlorophosphine, $NMe_2\cdot C_6H_4\cdot PCl_2$, is primarily formed, since sodium carbonate converts the product into a mixture (with dimethylaniline) of *tetramethyldiaminodiphenylphosphine oxide*, $(NMe_2\cdot C_6H_4)_2PHO$, m. p. 169° (insoluble), and dimethylaminophenylphosphinic acid (soluble, and stable towards boiling water; cf. Michaelis and Schenk, A., 1888, 834). The above oxide, in presence of water and air, gives tetramethyldiaminodiphenylphosphinic acid (m. p. 249—250° on Maquenne block, or 199° [decomp.] in capillary tube), the latter being formed, together with *hexamethyltriaminotriphenylphosphine dihydroxide*, $(NMe_2\cdot C_6H_4)_3P(OH)_2$, (m. p. 321° on Maquenne block) in the original condensation.

Diethylaniline and phosphorus trichloride give non-crystalline products.

Dimethylaniline (4 mols.), when heated with 1 mol. of phosphorus oxychloride at 130°, the product then being treated with sodium hydroxide, gives a mixture of (1) tetramethyldiaminodiphenylphosphinic acid, affording dimethylaniline when heated with calcium carbonate or with mineral acids; *sodium* salt,

$$(NMe_2\cdot C_6H_4)_2P(ONa)\colon O,H_2O;$$

(2) tetramethyldiaminodiphenylmethane, and (3) *hexamethyltriaminotriphenylphosphine oxide*, m. p. 262°, and the corresponding hydroxide (cf. *supra*).

Diethylaniline is converted by phosphorus oxychloride into *tetraethyldiaminodiphenylphosphinic* acid (m. p. 195° [decomp.] or 253—254° on Maquenne block), which is decomposed on heating with calcium carbonate or with mineral acids to give diethylaniline; it forms a *dihydrochloride* (hygroscopic, m. p. 185° on Maquenne block), a *sodium* salt (crystallising with 6 or $7H_2O$), and a *barium* salt.

Orthophosphoric acid and aniline give only aniline pyrophosphate.

E. E. T.

Studies Concerning the Direct Preparation of Organo-beryllium Halides. H. GILMAN (*J. Amer. Chem. Soc.*, 1923, **45**, 2693—2695).—Metallic beryllium, even when freshly cleaned by treatment with very dilute pure nitric acid, does not react with methyl iodide, ethyl iodide, benzyl bromide, bromobenzene, chlorobenzene, or α-bromonaphthalene, using as solvents anhydrous ether, anisole, benzene, or β-ethoxynaphthalene, and as catalysts iodine, bromine, dimethylaniline, ethyl acetate, or freshly prepared Grignard reagent. Experiments in which freshly sublimed beryllium iodide was used, and one in which the reaction mixture was exposed to *X*-rays, were also unsuccessful. W. S. N.

Action of Polyhalogenated Derivatives of Methane and Ethane on Magnesyl [Magnesium Alkyl] Compounds. III. R. BINAGHI (*Gazzetta*, 1923, **53**, 879—887; cf. A., 1922, i, 313, 1002).—Towards magnesium ethyl bromide, tetrachloromethane behaves similarly to chloroform, giving only ethylene and methane. With magnesium phenyl bromide, however, it yields, not tetraphenylmethane, but hexaphenylethane, triphenylmethyl peroxide, and triphenylcarbinol. This reaction exhibits marked analogy to the formation of hexaphenylethane by the action of zinc on triphenylchloromethane (cf. Gomberg, A., 1901, i, 77, 638; 1913, i, 259), which is yielded by the first phase of the reaction $3MgPhBr+CCl_4=CPh_3Cl+3MgBrCl$. The latter compound then reacts with another molecule of magnesium phenyl bromide, giving hexaphenylethane and bromobenzene, which also occurs among the products of the reaction $2CPh_3Cl+MgPhBr=MgCl_2+PhBr+CPh_3\cdot CPh_3$. That the reaction proceeds thus is confirmed by the simultaneous formation of triphenylcarbinol, which, under the experimental conditions employed, could not arise except by the hydrolysis of the triphenylchloromethane either by the water added to precipitate the basic magnesium salt or by the current of steam used to remove the bromobenzene and diphenyl. Atmospheric oxidation of hexaphenylethane explains the formation of triphenylmethyl peroxide, which is not obtained when an atmosphere of hydrogen is employed.

In the reaction between magnesium ethyl bromide and tetrachloromethane, the first phase consists of the addition of four molecules of the magnesium alkyl compound to one molecule of the methane derivative, evolution of gases occurring only when the product of the reaction is either left for some time or heated: $CCl_4+4MgEtBr=4MgClBr+4C_2H_4+CH_4$.

Triphenylmethyl peroxide, $O{:}O(CPh_3)_2$, forms a lustrous, white, microcrystalline powder, m. p. 186°, and yields rather low values for the molecular weight in freezing naphthalene. By dissolution in cold, concentrated sulphuric acid and subsequent addition of the solution to ice, triphenylcarbinol is obtained. Its *hexanitro-derivative*, $O{:}O[C(C_6H_4{\cdot}NO_2)_3]_2$, has m. p. 208—210°. T. H. P.

Arsino-arylamino-alcohols. C. W. Rodewald and R. Adams (*J. Amer. Chem. Soc.*, 1923, **45**, 3102—3105).—Amino-arylarsinic acids on condensation with β-chloroethyl and γ-chloropropyl chloroformates yield ω-chloroalkyl-(arsino-aryl)carbamates. On treatment with two molecular equivalents of aqueous alkali, the β-chloroethyl compounds are converted into arsino-aryl oxazolidones and the γ-chloropropyl compounds into 3-arsino-aryl-tetrahydro-1 : 3 : 2-oxazones. Excess of alkali hydrolyses the oxazolidones to β-arsino-aryl amino-ethanols and the oxazones to γ-arsino-aryl-aminopropanols. β-*Chloroethyl* (p-*arsinophenyl*)*carbamate*,

$$C_6H_4(AsH_2O_3)NH{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2Cl,$$

has m. p. above 250°, the corresponding (o-*arsinophenyl*)*carbamate* having m. p. 156—157°. β-*Chloroethyl* (2-*methyl*-5-*arsinophenyl*)*carbamate* has m. p. 193—195°. The γ-*chloropropyl* (p-*arsinophenyl*)*carbamate*, $C_6H_4(AsH_2O_3)NH{\cdot}CO_2{\cdot}[CH_2]_3{\cdot}Cl$, and the corresponding o-*arsinophenylcarbamate* melt at 245—246° and 130—132°, respectively. γ-*Chloropropyl* (2-*methyl*-5-*arsinophenyl*)*carbamate* has m. p. 160—162°. 3-p-*Arsinophenyl*-2-*oxazolidone*, $C_6H_4(AsH_2O_3){\cdot}N{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2$, forms colourless plates, m. p. above 280°.

3-o-*Arsinophenyl*-2-*oxazolidone* crystallises in colourless plates, m. p. 212—213°. 3-p-*Arsinophenyl*-1 : 3 : 2-*oxazone*,

$$C_6H_4(AsH_2O_3){\cdot}N{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2,$$

crystallises in white plates, m. p. 245—247°. β-(p-*Arsinophenyl*)-*aminoethanol*, $C_6H_4(AsH_2O_3)NH{\cdot}CH_2{\cdot}CH_2OH$, has m. p. 173—174°; the corresponding o-*arsinophenyl* derivative has m. p. 144—146°. β-(2-*Methyl*-5-*arsinophenyl*)*aminoethanol* has m. p. 144—146°. γ-(p-*Arsinophenyl*)*aminopropanol* has m. p. 167—168°; the similar o-*arsinophenyl* compound has m. p. 84—85°. γ-(2-*Methyl*-5-*arsinophenyl*)*aminopropanol* melts at 142—143°. p-*Arsinophenyl*-β-*hydroxyethyl nitrosoamine*, $C_6H_4(AsH_2O_3)N(NO){\cdot}CH_2{\cdot}CH_2OH$, is obtained from the corresponding aminoethanol and nitrous acid. It crystallises in bright yellow needles, m. p. 236°. p-*Arsinophenyl*-γ-*hydroxypropyl nitrosoamine*, $C_6H_4(AsH_2O_3)N(NO)CH_2{\cdot}CH_2{\cdot}CH_2OH$, is prepared similarly. It forms yellow crystals, m. p. 142—143°. The arsino-aryl-amino-alcohols are much less toxic than the corresponding arsanilic acids. F. G. P.

The Protein Matter of Bile. J. F. Logan (*J. Biol. Chem.*, 1923, **58**, 17—32).—Attempts have been made by various methods to isolate a pure protein from ox bile, and elementary analyses have been made of several of the preparations obtained. The results, however, indicate that, in each case, the product was probably a mixture of glucoprotein with a small amount of nucleoprotein. Direct acid hydrolysis did not liberate a reducing carbohydrate, but when this followed preliminary treatment with alkali the product had slight reducing properties. E. S.

Proteins of Wheat Bran. I. Isolation and Elementary Analyses of a Globulin, Albumin, and Prolamine. D. B. JONES and C. E. F. GERSDORFF (*J. Biol. Chem.*, 1923, **58**, 117—131).—Wheat bran, as free as possible from other portions of the wheat kernel, has been found to contain 17·25% of protein ($N \times 6{\cdot}25$). By extracting the bran successively with water, 4% sodium chloride, 70% alcohol, and 0·5% sodium hydroxide, 86·61% of the total protein has been removed and an albumin, a globulin, and an alcohol-soluble protein (prolamine) have been isolated from the first three extracts. Elementary analyses gave the following results: albumin, C=53·21, H=6·71, N=15·42, S=1·35%; globulin, C=53·43, H=7·40, N=17·76, S=0·91%; prolamine, C=54·25, H=6·75, N=15·35, S=1·35%. E. S.

Theory of Vegetable Tanning. II. Dehydration of the Gelatin Sol by Tannic Acid, Crystalline Tannins, and Simpler Phenols. H. G. B. DE JONG (*Rec. trav. chim.*, 1924, **43**, 35—67; cf. A., 1923, i, 821).—The stability of a gelatin sol is governed by two factors, electric charge and hydration. At the isoelectric point, p_H =4·7, the gelatin sol is uncharged, but retains its stability above the gelation temperature (about 40°) on account of its hydration. Increase of the hydrogen-ion concentration causes the particles to assume a positive charge, up to a maximum, beyond which the charge decreases. In the same way, decrease of the hydrogen-ion concentration imparts a negative charge to the particles up to a point, beyond which discharge takes place. Isoelectric or discharged sols can be coagulated by addition of dehydrating substances such as alcohol. Hydration changes in a sol can be followed by viscosity measurements, although the charge can also influence the viscosity (the quasi-viscous effect). This view of gelatin sols, it is claimed, expresses their behaviour better than the view which regards them as ion disperse systems.

It is shown by viscosimetric measurements that gelatin sols at 40° obey Poiseuille's law, and that the viscosity minimum is situated, at 40°, at the isoelectric point. The effect of tannic acid and phenols on gelatin sols was studied viscosimetrically at this temperature at different hydrogen-ion concentrations. At a small concentration of hydrochloric acid (0·003*N*), tannic acid has a marked dehydrating action, indicated by a lowering of the viscosity, but no precipitation occurs. At the isoelectric point tannic acid has both a dehydrating and a positive charging action on account of its own slight acidity. Consequently the viscosity minimum of a gelatin sol containing tannic acid lies at a small nominal concentration of alkali, which serves to restore the medium to the p_H of the isoelectric point. Further addition of alkali causes a powerful rehydration. The dehydration is relatively greatest at the isoelectric point, and, if pushed far enough, causes coagulation. The primary action of tannic acid on gelatin sols is therefore the same as on agar sols (*loc. cit.*). Phenol, pyrocatechol, resorcinol, quinol, pyrogallol, phloroglucinol, and ethyl gallate all have a similar dehydrating action on gelatin sols, the dehydrating action increasing rapidly with the number of phenolic groups. In the case of the two crystalline tannins, *d*-catechin and hamameli tannin, the dehydration is more powerful than with the simpler phenolic compounds. In the case of digalloylglucose, however, the positively charging influence of the tannin, tending to increase the viscosity, exceeds the dehydrating action, tending to lower the viscosity, at the isoelectric point, so that the viscosity is actually raised. However, a little sodium hydroxide in this case causes complete coagulation. Picric acid added to an isoelectric gelatin sol exerts at first a positively charging action, but with greater concentrations dehydration becomes very powerful, the positively charging action decreases, and finally precipitation occurs. Sodium picrate has no dehydrating action. E. H. R.

Gradual Decomposition of Proteins. Partial Hydrolysis of Keratin (Hog Bristles). E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1924, **132**, 1—11).—Hog bristles (400 g.) were heated with 1% hydrochloric acid (2 litres) in an autoclave at 120° for five hours, the product was neutralised with ammonia and then evaporated to dryness, mixed with sand and extracted with ethyl acetate. From the extract there were obtained *d*-alanylglycine anhydride, m. p. 250° (decomp.); prolyl-leucine anhydride, m. p. 158°, $[\alpha]_D^{20}$ −46·3° (in alcohol) (apparently partly racemised); l-*prolyl*-d-*valine anhydride*, m. p. 250—252°, and a *compound*, $C_{14}H_{23}O_3N_3$, m. p. 180—182°, which yields, on hydrolysis, proline, leucine, and alanine, and is formed from these by the loss of 3 mols. of water. From the product of the hydrolysis of hog bristles, using 70% sulphuric acid for seven days, the only pure compound isolated was l-*leucylserine*, $[\alpha]_D^{21}$ −44·3° (in water), and from the product of the hydrolysis by 70% sulphuric acid for fourteen days, a *valylvaline*, m. p. 255—260°, $[\alpha]_D^{20}$ +3·5° (in water), was obtained. In both cases, however, other scission products were shown to be present. W. O. K.

Biochemistry.

Iron Content of the Blood and Spleen in Infectious Equine Anæmia. L. H. WRIGHT (*J. Agric. Res.*, 1923, **26**, 239—242).—Analyses of the blood and spleens of a number of normal and anæmic animals are given. It would appear that the average total of the solids—iron, hæmoglobin, and erythrocytes—is considerably greater in the case of normal horses. Anæmia is indicated more by a lack of iron, and therefore of hæmoglobin, than by the number of erythrocytes. The increased iron content of the spleens of young horses is not considered to be entirely due to the larger amount of blood in the organ. A. G. P.

Relation between the Phosphate in Blood and Urine. V. B. Wigglesworth and C. E. Woodrow (*Proc. Roy. Soc.*, 1924, **B**, **95**, 558—570).—After the ingestion of acid or of alkaline sodium phosphate containing 1·5—2 g. of phosphorus, there is a 50—60% increase in the phosphate content of the blood, and simultaneously a large increase in the urinary phosphate. The urinary excretion of phosphorus is roughly proportional to the excess of phosphate above a certain value in the blood. Little change in the rate of excretion of phosphorus is caused by large variations in the amount of water excreted. The plasma and corpuscles normally contain equal amounts of inorganic phosphate, but when the phosphate in the whole blood is increased, that in the plasma exceeds that in the corpuscles. The organic fraction of the acid-soluble phosphorus does not increase after phosphate ingestion, or after ingestion of glucose with or without phosphate. W. O. K.

Some Experiments and Remarks on the Possible Transformation of *d*-Glucose in the Intestine and on the Nature of the Blood-sugar. S. Van Creveld (*Biochem. J.*, 1923, **17**, 860—871).—In agreement with Stiven and Reid (A., 1923, i, 1153), the observations of Hewitt and Pryde (A., 1920, i, 648) have not been confirmed. Using the aqueous humour of the eye and the blood-serum ultra-filtrate, it is shown that, although the former fluid when freshly collected decolorises potassium permanganate, neither fluid shows any mutarotation, and the copper-reducing value and the rotatory power are in close correspondence. In general, from the author's observations, no experimental support is forthcoming for the view that "reactive" sugars are intermediate metabolites, but the view that such may possibly occur is not abandoned. J. P.

The Absence of Effect of Insulin on the Heat Production in Isolated Frog's Muscle. R. Azuma and W. Hartree (*Biochem. J.*, 1923, **17**, 875—877).—Insulin has no effect either on the initial or on the recovery heat production of the isolated sartorius muscle of the frog. Injection of insulin into the intact frog produces convulsions which are relieved by glucose administration. J. P.

Studies on Carbohydrate Metabolism. II. On the Preparation of an Anti-diabetic Hormone from Yeast. I. H. B. Hutchinson, W. Smith, and L. B. Winter (*Biochem. J.*, 1923, **17**, 683—692).—A glucokinetic substance with physiological reactions closely resembling those of insulin may be extracted from yeast by methods similar to those used for preparing the pancreatic hormone. The lowering of blood-sugar may be followed by convulsions which are relieved by glucose injections. Various yeasts give very variable results, and only in the case of active yeasts does the activity increase on culturing. J. P.

Studies on Carbohydrate Metabolism. III. On the Formation of an Anti-diabetic Hormone by the Action of a Bacillus. (Preliminary Communication.) H. B. Hutchinson, W. Smith, and L. B. Winter (*Biochem. J.*, 1923, **17**, 764—767).—Injection into rabbits of an extract of the medium in which cultures of a coliform bacillus from yeast had been grown, produced hypoglycæmia and convulsions which were relieved by glucose administration. J. P.

The Transformation of Creatine into Creatinine. A. Hahn and L. Schäfer (*Z. Biol.*, 1924, **80**, 195—210).—A series of experiments on rabbits and on human beings shows that neither oral administration nor subcutaneous injection of creatine causes an increased output of creatinine. Of the creatine administered, a variable proportion appears in the urine; the fate of the remainder is unknown. The transformation of creatine into creatinine is a function of the muscles, and depends on the physico-chemical conditions there obtaining (probably the most important being the hydrogen-ion concentration), and not on the action of an enzyme. C. R. H.

The Fate of Indolepropionic Acid in the Animal Organism. F. W. Ward (*Biochem. J.*, 1923, **17**, 907—915).—Indolepropionic acid was prepared by the anaërobic action of a mixed culture of *Bacillus coli*, *B. chauvei*, *B. sporogenes*, and *B. œdemaciens* on tryptophan (cf. Hopkins and Cole, A., 1903, i, 590). Intravenous injection of indolepropionic acid gives rise to a keto or enol form of a 2-hydroxyindole compound. Indole-ethyl alcohol is oxidised to indole-acetic acid, whilst indolecarboxylic acid is excreted unchanged as a conjugated compound, and is therefore not an intermediate step in the oxidation of indolepropionic acid. J. P.

Experiments with Two Methods for the Study of Vitamin-*B*. H. C. Sherman and Harriet Edgeworth (*J. Amer. Chem. Soc.*, 1923, **45**, 2712—2718).—The importance of vitamin-*B* as a factor in food values makes it desirable that quantitative methods of known precision be applied in all studies of the vitamin contents of different foods. The gravimetric yeast-growth method was employed, using the Williams medium, and dried skimmed milk was used as the source of the vitamin. The growth was continued for thirty hours at 18°, being then arrested by the addition of formaldehyde. Consistent results were obtained, the probable errors being of the order of 1% of the observed numerical values. The method is open to the objection that the increased growth measured may be due to the introduction of other substances favourable to yeast-growth. The rat-growth method was also used and gave quantitative results, the probable error being in this case 2—4% of the numerical values. F. G. P.

A Critical Investigation and an Application of the Rat-growth Method for the Study of Vitamin-*B*. H. C. Sherman and Adelaide Spohn (*J. Amer. Chem. Soc.*, 1923, **45**, 2719—2728).—The rats used were fed on basal diets designed to be devoid of vitamin-*B*, and to contain all the other essential food factors in as nearly as possible the optimum proportions. Variations in the basal diets were made, fixed amounts of milk being used as sources of vitamin. It appears to be established from the results obtained that all increases of growth resulting from the addition of the milk to the basal diets used may be attributed to the vitamin-*B* thus furnished. There is no evidence of any measurable diminution of vitamin-*B* in milk powder heated dry at 100°, with free access of air. Probably about one-fourth of the vitamin is destroyed when the milk is heated in the fluid state for six hours at 100°.

F. G. P.

A Quantitative Study of the Destruction of Vitamin-*B* by Heat. H. C. Sherman and M. R. Grose (*J. Amer. Chem. Soc.*, 1923, **45**, 2728—2738).—The juice of canned tomatoes was used as a source of vitamin-*B* in this investigation, and the effect of heating at 10° intervals over the range of 100—130° has been examined, using the rat-growth method (see preceding abstract) as a measure of the vitamin content. At 100°, in a slightly acid medium, there is an appreciable destruction of the vitamin, and the results obtained at different temperatures show that the temperature coefficient of the destructive process is distinctly lower than that of most chemical reactions, resembling, in this respect, that of vitamin-*C*. It is therefore improbable that the vitamin is an unstable protein, and inappropriate to group it with enzymes, since typical enzymes have shown rates of destruction by heat with high temperature coefficients up to the point at which the enzymic activity was entirely destroyed. F. G. P.

A Preliminary Note on the Destruction of Vitamin-*B* by Age. G. M. Findlay (*Biochem. J.*, 1923, **17**, 887—890).—Indian lentils and peas which had been kept for thirty-eight years and had lost their power of germination showed, when fed to rats, a slight loss of vitamin-*B* in comparison with recent samples of these seeds.

J. P.

The Alleged Specific Colour Reaction for the Antiscorbutic Factor. H. D. Kay and S. S. Zilva (*Biochem. J.*, 1923, **17**, 872—874).—The blue colour given by the Bezssonoff reagent (*Bull. Soc. Chim. biol.*, 1922, **4**, 83) with certain preparations of the antiscorbutic vitamin is not specific. The constituent responsible for the coloration is, like the vitamin, destroyed by oxidation.

J. P.

Contributions towards the Study of the Lipoids of the Human Brain. F. Popescu (*Bul. Soc. Chim. România*, 1923, **5**, 83—92).—The author describes in detail the isolation of the lipoids present in the human brain, and extends the general methods for the determination of lipoids in blood (Grimbert and Laudet, A., 1913, ii, 164) to this case. A new method for the desiccation of the brain by means of freezing is described. After complete freezing, the brain is maintained at 40° for half an hour and the soft paste so obtained dried rapidly and completely in a vacuum. Extraction of the dried powder with acetone removes cholesterol, fats, and the phosphatides. The cholesterol separates from the hot extract on cooling, and is removed by filtration. The whole of the cholesterol present in the brain is found to exist in the free state and not combined with oleic acid. From the residue, a new *lipoid*, of the phosphatide group, having the composition $C = 67\cdot02\%$, $H=9\cdot93\%$, $N=2\cdot50\%$, $P=0\cdot534\%$, was isolated. This is soluble in alcohol and acetone, insoluble in cold ether, is precipitated by cadmium chloride, and gives no reaction with nitric or sulphuric acid. The solution of the lipoids remaining is precipitated with lead acetate, and yields mainly lecithin and a small quantity of kephalin. The residue from the acetone extraction is extracted with light petroleum; addition of alcohol to the concentrated extract precipitates kephalin (7—8%), and the alcoholic solution contains lecithin (5·5%).

The residue insoluble in acetone and light petroleum is finally extracted with alcohol, and this extract yields the substances contained in the grey matter (protagon), sphingomyelin (containing phosphorus) and phrenosin, and kerasin (phosphorus-free).

The determination of the lipoids present in a tubercular brain shows that the quantity of cholesterol is larger, and the quantity of other lipoids smaller, than in the normal brain.

For details of the separation and determination, the original paper must be consulted. J. W. B.

Gradual Decomposition of Proteins. Partial Hydrolysis of Keratin (Hog Bristles). E. Abderhalden and E. Komm.—(See p. 343.)

Auto-histo-radiographic Method for the Detection in Organs of Injected Polonium. A. Lacassagne and (Mme.) J. S. Lattès (*Compt. rend.*, 1924, **178**, 488—490).—The authors have made use of the α-ray emission of polonium, and its relatively long period of disintegration of 140 days, to obtain auto-radiograms of organs capable of retaining it. A rabbit was injected with polonium salts and killed after six days. Thin sections of the principal organs were made and placed on the sensitive surface of a photographic plate. After several days' exposure, records were obtained of the distribution of polonium. Retention by the various organs was very unequal, being greatest in the organs of elimination.

A. B. H.

Researches on Cellular Disintegration. A. Nodon (*Compt. rend.*, 1924, **178**, 486—487).—It is shown that living organisms, vegetable and animal, exhibit radioactivity, which appears to be a function of the degree of vitality of the organism. The radioactivity varied with the nature of the organism, and was increased by sunlight. The conclusion is drawn that both the disintegration

of radium and that of the living cell have their origin in exterior ultra-radiations, also that the atoms constituting the living material must acquire special properties, which allow them to disintegrate in a manner similar to those of the radioactive elements.
A. B. H.

[Cellular Disintegration.] D. Berthelot (*Compt. rend.*, 1924, **178**, 487).—The author observed in 1909 and 1910 phenomena similar to those observed by Nodon (preceding abstract). These he found to be due solely to changes of humidity. A. B. H.

The Extraction of the Concretion Gland and Nephridium of *Cyclostoma elegans*. P. Quast (*Z. Biol.*, 1924, **80**, 211—222).—A qualitative analysis of the concretion gland indicated the presence of silicates among the inorganic constituents and of uric acid, xanthine, hypoxanthine, and adenine among the organic ones. In the nephridium were found creatinine and allantoin.
C. R. H.

On the Participation of a Peroxidase in the Appearance of the Pigment in *Drosophila melanogaster*, Loew. De Luna (*Compt. rend.*, 1924, **178**, 525—527).—It is shown that a peroxydase takes part in the pigmentation of *Drosophila*. The peroxydase has the same distribution as the pigment. The appearance of the pigment is a function of temperature if the quantities of oxygen and peroxydase are constant; anæsthetics retard pigmentation.
A. B. H.

The Extractives of *Eledone moschata*. D. Ackermann, F. Holtz, and F. Kutscher (*Z. Biol.*, 1924, **80**, 155—162).—From this organism the authors have isolated betaine, taurine, lactic acid, and in addition two new bases which are designated *eledonine* ($C_{14}H_{30}O_3N_2$) and *homoeledonine* ($C_{15}H_{32}O_3N_2$). They both give chloroaurates melting indefinitely at 225—235°. The formula previously given to crangonine (A., 1908, ii, 53) is revised and now becomes $C_{13}H_{28}O_3N_2$, so that these three bases would appear to be members of an homologous series. C. R. H.

The Extractives of *Holothuria tubulosa*. D. Ackermann, F. Holtz, and H. Reinwein (*Z. Biol.*, 1924, **80**, 163—170).—In addition to betaine, adenine, and lactic acid, there was obtained from the lysine fraction a *chloroaurate* (m. p. 134°) of a base isomeric with homoeledonine (see preceding abstract). This substance on hydrolysis with hydrochloric acid gives betaine, and has therefore been named betainogen. C. R. H.

The Extractives of *Mytilus edulis*. D. Ackermann (*Z. Biol.*, 1924, **80**, 193—194).—Adenine was obtained in the purine fraction, and in the filtrate from the phosphotungstic acid precipitation was found the cyclose mytilitol (A., 1921, i, 764). C. R. H.

Proteins of Milk-serum. Their Separation by the Acetone Method. M. Piettre (*Compt. rend.*, 1924, **178**, 333—335).—The milk is coagulated rapidly by shaking at 35° and adding rennet, drop by drop, until casein begins to separate in a flocculent condition, after which the serum is filtered off by suction. It is rendered feebly acid with hydrochloric acid, extracted with ether, and the residual liquid precipitated by means of acetone and filtered. The precipitate is digested with water, and $N/10$-hydrochloric acid added in sufficient quantity to precipitate the lactoglobulin, which is then collected (using a centrifuge) and found to have $[\alpha]_D$ $-31° 12'$ in aqueous sodium hydroxide solution. The clear filtrate on precipitating, *e.g.*, with alcohol, affords the pure lactalbumin, with $[\alpha]_D$ $-41{\cdot}23°$. Milk contains, on the average, 2·3 g. of globulin and 3·2 g. of albumin per l. E. E. T.

Observations on certain Reducing and Oxidising Reactions of Milk. P. Haas and T. G. Hill (*Biochem. J.*, 1923, **17**, 671—682).—There is present in milk an oxygen acceptor capable of reducing sodium nitrate to nitrite, to which the name "*atite*" is provisionally given, and also an oxygen donator bringing about the reverse conversion of nitrite to nitrate (cf. Bach, A., 1911, i, 759) which has been called "*itate.*" Atite is precipitated with the milk proteins, and, although thermolabile, is not regarded as being an enzyme. Unlike atite, which is most active in the absence of oxygen, itate is active only in its presence, but in its thermolability and precipitation reactions it resembles the former. Both substances require an accelerator, aldehydes, notably acetaldehyde, being most active. Acetaldehyde in the presence of oxygen destroys both atite and itate. The diminution in the peroxydase reaction of milk is parallel to the rate of destruction of itate, and the possible identity of the last with peroxydase is considered. Atite is distinct from Schardinger's reductase. J. P.

The Protein Matter of Bile. J. F. Logan.—(See p. 341.)

The Occurrence of Amines in Urine. P. N. van Eck (*Pharm. Weekblad*, 1924, **61**, 65—73).—In testing samples of urine for blood, it was occasionally observed that a beautiful orange-red colour developed on addition of benzidine and glacial acetic acid, and before the addition of hydrogen peroxide. Out of 61 samples of urine, 25 gave positive results. Investigation failed to show that this was due to any specific malady or remedy. Negative tests were obtained with some twenty substances likely to be present in urine, and with the extracts obtained by shaking urine with the ordinary organic solvents. It was found, however, that the distillates from many urines gave the reaction, and contained alkylamines; the lower alkylamines were then examined, and all gave the reaction. By testing urine from healthy persons it was found that a positive result always followed a meal of pickled herrings, in which amines were identified, and that amines could be identified in the distillates from these urines, by the *iso*nitrile and nitroprusside reactions.

A collection of observations on the occurrence of alkylamines in animal and vegetable matter from various sources is given.

S. I. L.

Camphorylcarbamates and their Physiological Action. H. E. Fierz-David and W. Müller.—(See i, 301.)

The Physiological Effect of Gossypol. P. Menaul (*J. Agric. Res.*, 1923, **26**, 233—237).—The toxic effect of gossypol on rabbits was slow to appear if the substance was given with the food, but when it was injected directly into the blood-stream, the effects were apparent almost at once. It was found that gossypol prevents the normal oxygen-interchange in the blood, and also has a hæmolytic effect. Death is caused by a reduced oxygen-carrying power of the blood, which considerably increases the work of the respiratory and circulatory organs. This explained the condition of dead animals, viz., a passive hyperæmia and œdema of the lungs and some hydrothorax, which is directly due to the effect of gossypol and does not result from bacterial action. A. G. P.

Hypnotic Properties of Hydrobenzoin and of its Alkylated Homologues (Symmetrical Diarylglycols). Relations between Physiological Activity and Molecular Weight. M. Tiffeneau and C. Torres (*Compt. rend.*, 1924, **178**, 237—239).—The hypnotic effect, on the stickleback, of hydrobenzoin, and of its methyl, ethyl, *iso*propyl, butyl, *iso*butyl, and *iso*amyl derivatives has been measured (cf. A., 1923, i, 676). It is concluded that the hypnotic effect and molecular weight increase together. When, in a series (*e.g.*, in the present one, at the *iso*amyl member) the solubility limit is reached, the hypnotic effect then decreases as the molecular weight increases, unless biliary substances are added to promote absorption by the organism. E. E. T.

Constitution and Mode of Action of Biochemical Catalysts or Enzymes. Effects of Electrolysis on Enzymes of Pancreatic Juice and on the Amylase of Germinated Barley. F. Maignon (*Compt. rend.*, 1924, **178**, 420—423).—Preparations of the enzymes from the pancreatic juice of the cow, and of amylase from barley have been found to contain calcium, iron, and chlorine. On being electrolysed in aqueous solution, coagulation sets in near the anode, but not near the cathode. Finally, coagulation ceases, and the enzyme is found to be inactive, owing to removal of the inorganic constituents by electrolysis. The author concludes that the chlorine-ion is attached to the proteinic micellæ, the kations (Fe and Ca) being free in the liquid medium. In the case of hydrion, the latter is adsorbed on the external surface of the micellæ, this explaining (on ordinary adsorption theories) the great catalytic activity of that hydrion. E. E. T.

The Azine and Azonium Compounds of the Proteolytic Enzymes. I. H. R. Marston (*Biochem. J.*, 1923, **17**, 851—859).—Dyes of the azine group (eurhodines, safranines, indulines), but not their leuco-bases, quantitatively precipitate the proteolytic enzymes pepsin, trypsin, erepsin, and papain from their solutions. The enzyme is regarded as attaching itself to the azine nitrogen atom or atoms. Pepsin may be recovered in solution from the pepsin-azine precipitate by treatment with 0·5% hydrochloric acid and removal of the dye by extraction with amyl alcohol. It is suggested that the proteolytic enzymes may become attached to proteins, preliminary to hydrolysing them, through the nitrogen atoms of diketopiperazine groupings, and the results are interpreted in favour of the view that such groupings are present in the protein molecule. J. P.

Further Studies on the Enzymic Degradation of Polypeptides Composed of Amino-acids not yet found among the Degradation Products of the Proteins. E. ABDERHALDEN and A. MOSCHINI (*Fermentforschung*, 1923, 7, 176—178).—Yeast maceration juice degrades *d*-*n*-valyl-*l*-tyrosine but not *l*-*n*-valyl-*l*-tyrosine. In the former case, the formation of tyrosine and *d*-α-amino-*n*-valeric acid was demonstrated. The dipeptides were synthesised by combining *l*-tyrosine or its ester with *d*- or *l*-α-bromo-*n*-valeryl chloride. S. S. Z.

The Action of Enzyme Solutions on 3 : 5-Di-iodo-*l*-tyrosine and Glycyl-3 : 5-di-iodo-*l*-tyrosine. E. ABDERHALDEN and W. STIX (*Fermentforschung*, 1923, 7, 179—182).—Yeast maceration juice effects a cleavage in glycyl-3 : 5-di-iodo-*l*-tyrosine. Extract of pancreas and of the mucous membrane of the stomach do the same, but more slowly. Thyroid extract and thyroid press-juice have no action on the compound. S. S. Z.

The Action of the Enzymes of the Gastro-intestinal Tract on Diketopiperazine. E. ABDERHALDEN and K. GOTO (*Fermentforschung*, 1923, 7, 169—175).—It is concluded that neither trypsin nor pepsin has an appreciable hydrolytic action on *d*-alanylglycine anhydride, and that the hydrolysis which is effected by alkaline or acid solutions of these enzymes is due to that alkalinity or acidity. The anhydride was obtained by hydrolysing silk resides. S. S. Z.

Urease. II. The Mechanism of the Zymolysis of Urea. W. R. FEARON (*Biochem. J.*, 1923, 17, 800—812).—Using the method described by the author (A., 1923, i, 497), it is shown that cyanic acid and ammonia, but not carbamic acid, are intermediate products of the zymolysis of urea (cf. Mack and Villars, A., 1923, i, 405). Soja urease, which carries a negative electric charge, adsorbs urea from alcoholic solution and ammonia from aqueous solution. It is concluded that urease adsorbs its substrate, and that the adsorbed urea is then decomposed into ammonia and cyanic acid. The former is readsorbed as such by the enzyme and the latter is hydrolysed by the solvent water. The enzyme is again liberated by combination of the adsorbed ammonia with ammonium hydrogen carbonate and is free to adsorb more urea. The cyclic process continues until arrested by accumulation of ammonium carbonate or by exhaustion of the substrate. J. P.

Studies on Enzyme Action. The Relationship between the Chemical Structure of certain Compounds and their Effect upon the Activity of Urease. E. W. ROCKWOOD and W. J. HUSA (*J. Amer. Chem. Soc.*, 1923, 45, 2678—2689).—The effect of various compounds on the activity of urease obtained from jack-bean meal has been studied, and the following results have been obtained.

Certain compounds exert a promoter effect on the catalytic activity of the urease, others have an inhibitory action. These effects are independent of changes in hydrogen-ion concentration. The promoter effect is related to the presence of both amino and carboxyl groups. Compounds containing only one of these groups were not promoters. The promoter action seems to be a function of the distance between the groups, all the α-amino-acids used being marked promoters, β-amino-acids having a slight effect, and γ-amino-acids none. With the aminobenzoic acids, the order of decreasing effect is ortho, meta, para. A second amino or carboxyl group in an α-amino-acid increases the promoter action. α-Amino-acids of the heterocyclic nitrogen compounds have a slightly greater effect than simple α-amino-acids. Ammonium chloride, guanidine sulphate, creatine, and creatinine have no promoter effect. Enzymes appear to be of a protein nature or to occur associated with protein, and when the protein is removed from the enzyme solution, the activity is lost. The experiments which show the promoter action of α-amino-acids and peptones indicate that the protein part of enzyme preparations is an important factor in the action of the enzyme. The results obtained also tend to disprove the hypothesis that the promoter effect is due chiefly to prevention of decomposition of the enzyme. F. G. P.

Experiments Demonstrating the Existence of Specific Cytolysins for the Various Organs of the Animal Organism. A. ZERKOWITZ (*Fermentforschung*, 1923, **7**, 223—228).—It is claimed that some of the experiments carried out with the blood sera of normal and castrated rabbits, and the testicles and other organs of these animals, confirm the author's hypothesis of the existence of specific cytolysins. S. S. Z.

Carbohydrate and Fat Metabolism in Yeast. I. S. MACLEAN and D. HOFFERT (*Biochem. J.*, 1923, **17**, 720—741).—Yeast incubated in oxygenated water shows a diminished carbohydrate content and an increase in fat. Propyl, butyl, and *iso*amyl alcohols inhibit this conversion, whilst the sodium salts of formic, propionic, and butyric acids, glycol, glycerol, and acetone, in 0·1*M*-solution, behave like water. Incubation in 0·5% solutions of ethyl alcohol, or of the sodium salts of acetic, lactic, and pyruvic acids gives the same results as 0·5% solutions of dextrose; in the first two cases increase of the total carbohydrate of the yeast-cell is observed. In the presence of dextrose, lævulose, and sucrose the yeast-cell stores both carbohydrate and fat. Maltose is exceptional in producing a greater carbohydrate and lesser fat storage than the other sugars investigated. It is suggested that maltose is assimilated as such by the yeast-cell. Continuous oxygenation during incubation greatly increases the amount of fat produced, but has little or no effect on the carbohydrate. In oxygenated solutions, added phosphate reduces the amount of carbohydrate stored and increases the fat formation. Phosphate is taken up by the cell in proportion to the sugar concentration of the solution; more phosphate is taken up from oxygenated than from non-oxygenated solutions. It is suggested that the formation of hexose phosphate is the first stage in the conversion of carbohydrate into fat. J. P.

Irregularities of the Lactic Fermentation in Presence of certain Antiseptics. A. Lumière (*Compt. rend.*, 1924, **178**, 258—260).—It is shown that the supposed irregularity observed by Richet (*ibid.*, 1923, **177**, 1262) in connexion with the antiseptic action of mercuric chloride is due to the use, by this author, of inocula from non-uniform bacterial suspensions. If the latter are well shaken, in order to break up large aggregates, perfectly uniform results are obtained with antiseptics. E. E. T.

Production of β-Hydroxybutyric Acid by Microbial Processes. M. Lemoigne (*Compt. rend.*, 1924, **178**, 253—256; cf. A., 1923, i, 881).—The alcoholic extract of fresh cultures of *Bacillus M.* gives, on evaporation and distillation of the residue, α-crotonic acid. β-Hydroxybutyric acid is therefore a normal physiological product of the bacillus, and is formed from intracellular reserve material. E. E. T.

Variations in Hydrogen-ion Concentration under the Influence of the Assimilation of Nitrates by *Aspergillus repens*, De Bary. Bach (*Compt. rend.*, 1924, **178**, 520—522).—When *Aspergillus repens*, De Bary, is allowed to grow in a suitable medium containing nitrates and for which p_H has an initial value between 3·6 and 8·4, the hydrogen-ion concentration after ten days approximates to the value $p_H = 6$. The addition of potassium phosphate reduces the rate of the change, but does not alter its sense. A. B. H.

The Accumulation and Formation of Urea in Mushrooms. N. N. Ivanov (*Biochem. Z.*, 1923, **143**, 62—74).—The urea content and nitrogen distribution in mushrooms, artificially cultivated in manure, has been estimated at various stages of growth. The dried fungi may contain up to 13% of urea. The amount of urea increases during the ripening process until spore formation begins, autolysis of the proteins and chitin leading to an increase in the amino compounds, which are then converted to urea. By treatment with chloroform, the formation of urea may be inhibited. The high urea content is ascribed to the artificial culture in the nitrogen-rich medium. A close analogy is drawn between the formation of urea and asparagine (cf. also A., 1923, i, 428, 520). J. P.

The Migration of Inulin in the Grafts of Composites. H. Colin and R. Franquet (*Compt. rend.*, 1924, **178**, 518—520).—It is shown that when a branch of a plant containing inulin is grafted on a subject which does not normally contain this substance, the latter migrates into the subject, but undergoes hydrolysis to lævulose. It is sometimes possible, however, to detect the inulin in the immediate vicinity of the graft. The optical rotations of the sugars above and below the graft are frequently in opposite direction. A. B. H.

The Acidity of Maize and its Relation to Vegetative Vigour. A. M. Hurd (*J. Agric. Res.*, 1923, **25**, 457—468).—Measurements of the hydrogen-ion concentration and titratable acidity of the expressed juice of maize plants, showed these two factors to vary inversely as the vigour of the plant. Alterations in sap density did not account for variations in acidity, with the exception of a few cases where particularly high values were obtained. The concentration of titratable acid in the leaf-juice was always greater than in the stalk, whatever the state of vigour of the plant. In vigorous plants, the p_H values of the leaf juices were greater than those of the stalk juices. This relationship was reversed in the case of weakly, stunted plants. The density of the juice of the leaves was greater than that of the stalks, whether the plant was vigorous or otherwise. Variations in the acidity of plants of the same strain but in a different environment were considerably greater than those of different varieties under similar conditions of growth and vigour. A. G. P.

On the Significance of the Ash Content of certain Marine Algæ. P. Haas and B. Russell-Wells (*Biochem. J.*, 1923, **17**, 696—706).—From a comparison of the sulphate content of the hydrolysed aqueous extracts of certain marine algæ (*Rhodophyceæ* and *Phæophyceæ*) with the sulphate content observed after incineration, it is found that the former is greater than the latter and frequently in the ratio 2 : 1. This is ascribed to the presence of a complex calcium organic sulphate of the type $R{<}\substack{O\cdot SO_2\cdot O\\ O\cdot SO_2\cdot O}{>}Ca$, in which the calcium, but not the sulphate, is freely ionised. These colloidal complexes have a measurable conductivity and osmotic properties to which considerable importance is attached (cf. Harwood, T., 1923, **123**, 2254). J. P.

On the Determinable Iodine of *Laminaria flexicaulis*. P. Freundler (*Compt. rend.*, 1924, **178**, 515—517).—The iodine content of perfectly fresh *Laminaria flexicaulis* has been determined by three methods. The author concludes that the alga contains, in addition to its normal iodide content, a fairly constant quantity of a substance of unknown composition which is transformed into iodide on the death of the organism. A. B. H.

Quantitative Diurnal Variation of Starch in Green Plant Leaves. P. P. Stanescu (*Compt. rend.*, 1924, **178**, 117—119).—The starch-content of green leaves has been determined hourly or half-hourly, successive strips being cut from the same leaf at these intervals, and extracted with boiling water and alcohol. At the end of the day, the leaf is reassembled, and developed by immersion in iodine–iodide solution. The variation of starch-content throughout the day is then clearly seen. With most leaves (particularly from March to July) a single daily starch maximum is observed (*Robinia pseudacacia*, etc.). In August and September, two maxima are often observed. Several maxima are rarely found (*Rhus typhina* showing five). With *Chelidonium majus* and *Atriplex patula*, maxima and minima succeed each other rhythmically, whilst with *Urtica dioica* starch suddenly appears and as suddenly disappears again. E. E. T.

Galuteolin, a New Glucoside from *Galega officinalis*. G. Barger and F. D. White (*Biochem. J.*, 1923, **17**, 836—838).—From the seeds of *Galega officinalis* a glucoside, $C_{21}H_{20}O_{11},3H_2O$, to which the name *galuteolin* is given, has been isolated. It contains no methoxyl groups. On hydrolysis, it yields dextrose and an insoluble yellow colouring matter decomposing at 290—300°, of the composition $C_{15}H_{10}O_6$, identified as luteolin, which, when boiled with acetic anhydride containing a trace of sulphuric acid or pyridine, forms a tetra-acetyl compound, $C_{15}H_6O_6(C_2H_3O)_4$, long, colourless needles, m. p. 221—223°. Luteolin occurs as such in the seeds of *Galega officinalis*. The temperatures at which hydroxyflavones such as luteolin sublime in a high vacuum are characteristic. J. P.

Localisation of the Cyanogenetic Glucosides in *Prunus occidentalis* and *P. myrtifolia*. E. Mameli-Calvino (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 423—430).—By means of Treub's Prussian blue reaction the author has established the localisation of a cyanogenetic glucoside in the bark and leaves of *Prunus occidentalis* and *P. myrtifolia*. Peche's mercurous nitrate method is unsuitable for this purpose, since the reagent may be reduced by the action of cellular constituents which yield no hydrocyanic acid. Microchemical investigation fails to reveal the presence of alkaloids in the bark or leaves of these two species. T. H. P.

A Labile Form of Protein and its Relation to Living Protoplasm. II. O. Loew (*Biochem. Z.*, 1923, **143**, 156—160).—The occurrence is described, in various vegetable cells, of rounded, highly refractive protein droplets resembling the "caffeine proteosomes" previously discovered by the author (A., 1915, i, 1079). These are coagulated by the vapour of ether and chloroform, and combine with bases to form insoluble stable complexes. They also combine readily with water and are made insoluble by neutral salt solutions and by hydrocyanic acid. The reactivity of these droplets is discussed in relation to protoplasmic activity. J. P.

Proteins of Wheat Bran. I. Isolation and Elementary Analyses of a Globulin, Albumin, and Prolamine. D. B. Jones and C. E. F. Gersdorff.—(See this vol., i, 342.)

Detection and Distribution of Phytosterols in Latex. G. Klein and K. Pirschle (*Biochem. Z.*, 1923, **143**, 457—472).—An improvement is effected in the method available for the extraction of phytosterols from dried plant residues, by shaking the extract dissolved in light petroleum with 50% aqueous sodium hydroxide, whereby the impurities, which render recrystallisation difficult, are hydrolysed and may be subsequently washed out with aqueous sodium carbonate and distilled water. Crystallisation of the phytosterols then proceeds readily. Euphorbone has been obtained in this way, not only from the *Euphorbiaceæ*, but also from many other latex-forming plants, and its nature as a phytosterol has been established by the digitonin test (cf. Windaus, A., 1910, ii, 462).

The presence of 0·1 to 2·0% of phytosterol in latex is regarded as characteristic. A *bromo*- (m. p. 83°) and a *nitro*-derivative of euphorbone are described; a benzoyl derivative was not obtained (cf. Emmerling, A., 1908, i, 438). The physiological significance of phytosterols is discussed. J. P.

A Crystalline Metabolic Product from *Sparassis ramosa*. R. Falck (*Ber.*, 1923, **56**, [*B*], 2555—2556).—Remarkable growth of crystals is observed in pure cultures of *Sparassis ramosa* both in the substrate and on the surface. On the latter they are formed as long needles, in the former as small, rounded crystalline aggregates. The substance possesses the power of protecting the cultures from impurities in a remarkable manner. It can be isolated almost quantitatively by distillation of the substrate with steam. Its constitution has been elucidated by Wedekind and Fleischer (this vol., i, 174), by whom it has been designated "sparassol." H. W.

The Effect of Physiologically Acid and Alkaline Nitrogenous Fertilisers. F. Münter (*Z. Pflanz. Düng.*, 1923, **A**, **2**, 497—516).—The results of pot trials of the effect of various fertilisers on the yield of wheat and linseed are reported. They confirm the conclusions of earlier experiments. Physiologically acid nitrogenous fertilisers such as ammonium sulphate increase the availability of phosphorus in sandy soils so long as the soil reaction remains alkaline. Where a soil contains very small quantities of calcium carbonate, ammonium sulphate may depress the yield. The production of "alkali" in the soil as a result of heavy dressings of sodium nitrate depresses the availability of phosphorus and crop yield. Flax is more sensitive to alkalinity than is wheat. G. W. R.

Physiological Function of Iodine in the Sugar-beet. J. Stoklasa (*Compt. rend.*, 1924, **178**, 120—122).—Iodine (present as potassium iodide), although inimical to many plants, is absorbed by the leaves and roots of the sugar-beet, the weight of the whole plant and the percentage sucrose content increasing as a result. The moderate use (about 2 lb. per acre) of potassium iodide as a practical fertiliser in sugar-beet growing is therefore to be recommended, this applying even in the second year. A too free use (*e.g.*, 4 lb. per acre) of iodide, however, diminishes the growth and sucrose content, some arabinose appearing in the roots. E. E. T.

Lysimetric Studies. Soil and Subsoil in Calcium–Magnesium Interchange. W. H. MacIntire, W. M. Shaw, and J. B. Young (*Soil Sci.*, 1923, **16**, 321—341; cf. A., 1923, i, 1168).—Further data are given in connexion with lysimetric studies on soils treated with different compounds of calcium and magnesium. It is shown that the general effect of calcium dressings is to depress the outgo of magnesium from the soil and to increase the outgo from the subsoil. Magnesium dressings have a similar effect on the outgo of calcium from soil and subsoil. G. W. R.

Organic Chemistry.

Physical Properties of the Paraffin Hydrocarbons. R. E. Wilson and W. H. Bahlke (*Ind. Eng. Chem.*, 1924, **16**, 115—122).—Curves are presented between the following physical properties: vapour pressure and temperature, heat of vaporisation and vapour pressure, liquid density and temperature, and specific heat and temperature for the paraffin hydrocarbons from butane to tetracosane. These are compiled from published data and corrected and extended as follows: the vapour-pressure curve by Hildebrand's generalisation that the slope of the curve for any liquid is a constant if the vapour concentration is constant, with application of a correction based on Young's data for the lower members of the series; the heat of vaporisation on Hildebrand's similar rule that the molal entropy of vaporisation for all normal liquids is the same at equal vapour concentrations; the liquid density curve by the theorem of corresponding states. The critical data are calculated from Young's results and from the vapour-pressure curve. Only scanty specific heat data are available. [Cf. *B.*, 1924, 243.] C. I.

Characteristics of the Hydrocarbons in [American] Mid-continent Kerosene. C. R. Wagner (*Ind. Eng. Chem.*, 1924, **16**, 135—136).—The distillate from Oklahoma crude petroleum contains paraffins only in the most volatile fractions. When treated with half its volume of liquid sulphur dioxide at − 10°, a fraction soluble in the latter is separated of similar boiling point but higher specific gravity, the proportion of this fraction to the whole rising with the boiling point. In the case of a kerosene, b. p. 198—244°, the SO_2-soluble fraction amounted to 5·4%. This fraction was subjected to repeated fractional distillation under reduced pressure, yielding four main fractions, the freezing points, indices of refraction, elementary analyses, and molecular weights of which were determined. The suggested formulæ are $C_{12}H_{18}$, $C_{14}H_{20}$, $C_{13}H_{18}$, and $C_{14}H_{18}$; it appears probable that these compounds are partly hydrogenated substituted naphthalenes. Their characteristic property, which is common to all SO_2-soluble fractions of this petroleum, is that they are readily nitrated even by dilute nitric acid. The SO_2-insoluble oil was similarly fractionated and examined. This fraction is unaffected by sulphuric acid ($d = 1·68$) and consists essentially of members of the *cyclo*hexane series. C. I.

Velocity of Oxidation of Paraffin Wax. I—IV. F. Francis [with W. F. Millard, C. H. Rutt, C. M. Watkins, R. W. Wallington, and C. P. Garner] (*J. Chem. Soc.*, 1924, **125**, 381—393).—Paraffin wax, obtained from shale oil and fusing at 55—56°, is oxidised exothermally by a stream of air or oxygen at 100—135°. Commencement of reaction is preceded by a latent period, after which the oxygen content rises to 11—16% in 70—1800 hours. The latent period may be reduced by heating the wax, previous to oxidation, in a sealed vacuum (a treatment which does not alter the physical constants of the material, but slightly increases its solubility in chloroform and acetone), by the use of catalysts, and by previous treatment with sulphuric acid at 100°, which causes a loss in weight of about 5% of the material. Wax which, after being heated in a vacuum, was recrystallised from acetone had the same latent period as the untreated material. The latent period may therefore be ascribed to (*a*) the formation of a positive catalyst, (*b*) the destruction of a negative catalyst present in the original wax, or (*c*) isomeric change brought about by the action of heat, particularly the formation of unsaturated substances (cf. T., 1922, **121**, 498, 1534). Commencement of the oxidation is marked by the formation of carbon dioxide, and formic acid is always produced in the later stages of the reaction. The oxidation in presence of catalysts appears to take place in stages.

Wax treated at 100° with a stream of oxygen required 1060 hours to attain an oxygen content of 7%; with air at 100° the latent period was too long to determine, but at 120° an oxygen content of 7% was reached after 285 hours. Untreated wax in the presence of 5% of turpentine reached an oxygen content of 7% in 800 hours with air and in 320 hours with oxygen at 100°, in 285 hours with air at 120°, and in 46 hours with oxygen at 135°.

The temperature coefficient of the oxidation with oxygen is 1·6, whilst that of the latent period is 2·9. These values suggest that the rate of oxidation is governed by a physical process, but that the latent period is accompanied by a chemical change. Wax from lignite, having m. p. 46—47°, and containing 0·7% of oxygen, commenced to oxidise with oxygen at 135° after 10 hours, and contained 7% of oxygen after 24 hours. F. G. W.

Action of Iodine on Hydrocarbons. F. J. Nellensteyn (*Chem. Weekblad*, 1924, **21**, 102—106).—Iodine acts on all hydrocarbons, sometimes in the cold, but generally at high temperatures, forming hydrogen iodide, with separation of carbon and formation of colloidal carbon solutions. Treatment of paraffin oil at 160° gave a coal-like product, some 70% of the iodine added being driven off, mostly as hydrogen iodide, partly as free iodine. Reaction occurred at the ordinary temperature with a distillate from a Borneo asphaltic oil, *d* 0·886, b. p. 192—300°; at 160°, the iodine was converted nearly quantitatively into hydrogen iodide, carbon being formed both as a precipitate and in the colloidal condition. The results are interpreted as indicating reaction of the iodine with dissociation products of the hydrocarbons, containing only one carbon atom, *e.g.* $CH_3\cdot$, $CH_2:$, and $CH\vdots$. A highly unsaturated "cracked" gas-oil distillate, *d* 0·866, b. p. 58—150°, reacted with iodine very strongly at the ordinary temperature; the carbon which separated contained 30—37% of adsorbed iodine, not removable by thiosulphate or sodium hydroxide, but partly removed by alcohol. A high adsorbing power is to be expected, since the carbon is formed at low temperatures. The action of iodine is therefore analogous to that of oxygen, in that hydrogen is removed from dissociation products containing only one atom of carbon, with separation of the latter in the colloidal condition, thus forming asphalt. S. I. L.

Acceleration of the Reaction between Ethylene and Sulphuric Acid. W. GLUUD and G. SCHNEIDER (*Ber.*, 1924, **57**, [*B*], 254—255).—The absorption of ethylene by sulphuric acid is catalytically accelerated by the presence of lead sulphate, calcium sulphate, ferric sulphate, anhydrous copper sulphate, or, particularly, ferric ammonium alum. The most suitable catalyst, however, is silver sulphate added to the extent of 0·5—1% of the weight of sulphuric acid; in contrast to the other catalysts, this material retains its activity over long periods, so that higher concentrations of ethyl hydrogen sulphate can be attained. It is readily recovered by electrolysis. H. W.

Contact Condensation of Acetylene. N. ZELINSKY (*Ber.*, 1924, **57**, [*B*], 264—276).—The pyrogenic condensation of acetylene in the presence of activated birch or lime charcoal has been studied; the adsorbent properties of the material give, in effect, the action of very greatly increased pressure without involving the dangers incurred in working with compressed acetylene. The method has the advantage that the temperature can be raised without danger to 600—650°, at which the process proceeds most advantageously, and that, in consequence of the presence of charcoal, the condensation occurs quietly and without explosion of the acetylene, which need not therefore be diluted with an indifferent gas. The deposition of carbonised matter on the contact material takes place to only a very minor extent, and the formation of solid hydrocarbons (cuprene) is not observed. Further hydrogenation of the aromatic hydrocarbons which are produced is scarcely observable. The main product of the change is benzene.

The most favourable conditions for the condensation of acetylene are secured when the gas is passed at the rate of 20 litres per hour through a hard glass tube, about 1 metre long and 1·5—2·4 cm. internal diameter, heated at 650°. The escaping gases consist mainly of acetylene containing some ethylene; the yield of tar exceeds 70% of that theoretically possible.

The tar is reddish-brown in colour and aromatic in odour. Colour and transparency depend considerably on the temperature and freshness of the contact agent. Its density varies according to the temperature of the experiment from 0·911 (600°) to 0·995 (660°), but never exceeds 1. It is separated by distillation into the following fractions: light oil, b. p. below 170°, 49·0% (45% below 150°); middle oil, b. p. 170—230°, 11·7%; heavy oil, b. p. 230—270°, 9·5%; anthracene oil, 21·2%; pitch, 6·8% (loss 1·8%). The preliminary fraction contains small amounts of diacetylene, CH:C·C:CH. The light oil consists mainly of benzene (35% of the tar) accompanied by small amounts of toluene and *p*-xylene (cf. A., 1923, i, 1169). The presence of styrene in the fraction, b. p. 140—150°, and of indene in the fraction, b. p. 150—180°, is established. The middle oil solidifies at the atmospheric temperature to a yellow, crystalline mass, impregnated with liquid; it contains chiefly naphthalene. The green heavy oil contains large quantities of crystals of fluorene. The red anthracene oil deposits the hydrocarbon freely at the atmospheric temperature.

Reduction of the portion of the light oil boiling below 150° in the presence of nickel gives a mixture of cyclic hydrocarbons in which *cyclo*hexane predominates; it has b. p. 70—110°, d_4^{20} 0·7805, n^{24} 1·4238.

Acetylene is rapidly converted at 650° in the presence of active platinised asbestos into a pale yellow, transparent, aromatic tar, the yield being 45—50%; a portion of the acetylene, however, suffers decomposition in such a manner that the catalyst becomes coated with soot which ultimately inhibits the reaction; the tar is characterised by its very low content (5%) in pitch. Palladised asbestos is unsuitable for the condensation of acetylene. In the presence of pure, ignited asbestos, condensation of acetylene takes place at 650° with the production of a viscous, black, aromatic tar, d^{19} 1·000; the yield is about 40%. The action proceeds quietly without explosion, but cannot be continued over long periods on account of the deposition of soot. H. W.

Derivatives of Δ^{α}-Butylene. M. DE MONTMOLLIN and P. MATILE (*Helv. Chim. Acta*, 1924, 7, 106—111).—By the action of cold aqueous hypochlorous acid on Δ^{α}-butylene, *butylene-α-chlorohydrin*, $CH_2Me{\cdot}CH(OH){\cdot}CH_2Cl$, is obtained as a colourless liquid, b. p. 141°. When oxidised with chromic acid, it gives chloromethyl ethyl ketone, a liquid with a pungent odour, b. p. 135—137°; this is also formed as a by-product with the butylenechlorohydrin, together with αβ-dichlorobutane and some higher chlorinated products, including (?)*αβγ-trichloro-*n*-butane*, b. p. 165—168°/725 mm. *Butylene α-bromohydrin*, prepared from α-butylene and hypobromous acid, is a colourless liquid, b. p. 56—58°/11 mm. By oxidation it gives bromomethyl ethyl ketone, b. p. 145°/725 mm. This ketone is also formed as a by-product with the bromohydrin, together with some αβ-dibromobutane and a *bromobutylene bromohydrin*, b. p. 79—80°. The above chloromethyl ethyl ketone gives with phenylhydrazine a *compound*, yellow crystals, m. p. 210—215° (decomp.), whilst bromomethyl ethyl ketone gives a *compound*, greenish-yellow crystals, m. p. 200—205° (decomp.). Both appear to contain two phenylhydrazine residues, and should be the same phenylhydrazido-phenylhydrazone; the difference cannot yet be explained.

α-Butylene diacetate is obtained by heating αβ-dibromobutane with fused potassium acetate and glacial acetic acid; it is a colourless liquid with an agreeable odour, b. p. 196—199°. When this liquid is saturated with gaseous hydrogen bromide, *α-bromo*-sec.-*butyl acetate*, $CH_2Me{\cdot}CH(OAc){\cdot}CH_2Br$, a pale yellow liquid, b. p. 76°/15 mm., is formed. *α-Butylene oxide*, $CH_2Me{\cdot}CH{<}\overset{CH_2}{\underset{O}{|}}$, is formed by the action of potassium hydroxide solution on the chloro- or bromo-hydrin; it is a colourless liquid, b. p. 58·5—59·0°. It is converted by 25% ammonia solution into *α-amino-*sec.*-butyl alcohol*, b. p. 168—170°.

E. H. R.

Alkaline Reduction of the Carbon Tetrahalides and of Potassium *aci*-Nitroform. R. O. GRIFFITH and L. HUNTER (*J. Chem. Soc.*, 1924, **125**, 463—464).—The carbon tetrahalides are effectively reduced by phenylhydrazine, arsenious oxide, or sulphites in alkaline solution. The action of acetone, hydrazine, antimonious oxide, and stannites is less certain. In the reduction of trichlorobromomethane to chloroform by means of aqueous sodium arsenite, dichlorobromomethane was not formed. Bromoform is reduced to methylene bromide by alkaline reagents, with the production of much formate, and chloroform is hydrolysed to formate without the production of methylene chloride. The action of alkaline reducing agents on potassium *aci*nitroform does not produce potassium dinitromethane, the salt being completely decomposed with the formation of ammonia. Hydrazine or phenylhydrazine reacts with evolution of nitrogen, a result which may explain the abnormally large production of nitrogen in the reaction between these compounds and tetranitromethane (T., 1923, **123**, 2305; and 1920, **117**, 880).

F. G. W.

Preparation and Reactions of the Dihalogenodinitromethanes. R. A. GOTTS and L. HUNTER (*J. Chem. Soc.*, 1924, **125**, 442—450).—The action of potassium hydroxide, iodide, cyanide, and nitrite, and of sodium thiosulphate, on the dihalogenodinitromethanes was investigated to test the hypothesis of Macbeth (T., 1922, **121**, 1118), that the activity of halogen atoms in similarly constituted molecules is the result of an induced positive polarity. In general, the stability of the compounds investigated conforms to the order $Cl > Br > I$, although in the case of the mixed dihalogenodinitromethanes exclusive removal of the more positive atom does not take place.

Potassium hydroxide reacts with dichloro- and dibromo-dinitromethanes according to the equation, $CCl_2(NO_2)_2 + 2KOH = CKCl(NO_2)_2 + KClO + H_2O$. In the case of chlorobromodinitromethane, the product is a mixture of the potassium salts of chloro- and bromo-dinitromethane. Chloroiododinitromethane behaves similarly to the chlorobromo-compound, losing more iodine than chlorine.

Potassium iodide reacts with the dihalogenodinitromethanes according to the equation, $CX_2(NO_2)_2 + 2KI = CKX(NO_2)_2 + KX + I_2$, both halogens being removed in part, but chlorobromodinitromethane gives also a small proportion of the iodo-salt.

Potassium cyanide behaves more energetically than the iodide, and both halogen atoms can be removed according to the equations, $CX_2(NO_2)_2 + KCN = CKX(NO_2)_2 + CNX$ and $2CKX(NO_2)_2 + 2KCN + H_2O = 2CKH(NO_2)_2 + KX + CNX + KCNO$; potassium chlorodinitromethane, however, remains unaffected on prolonged treatment with potassium cyanide.

Potassium nitrite acts as a reducing agent only in the case of chloroiododinitromethane, according to the equation, $CClI(NO_2)_2+2KNO_2=CKCl(NO_2)_2+KNO_3+NO+I$. The action of potassium nitrite in presence of carbonate on dibromodinitromethane is represented by the equations, $CBr_2(NO_2)_2+KNO_2+K_2CO_3=CK(NO_2)_3+KBr+KBrO+CO_2$, and $CBr_2(NO_2)_2+KNO_2+K_2CO_3=CKBr(NO_2)_2+KBr+KNO_3+CO_2$. Chlorobromodinitromethane yields the nitroform salt in much smaller proportion, and none is obtained from the dichloro-compound.

Sodium thiosulphate reduces potassium bromo- and iodo-dinitromethanes to potassium dinitromethane; the chloro salt is reduced much more slowly.

The action of acids on potassium bromodinitromethane is represented by the equation, $2CKBr(NO_2)_2+H_2SO_4=CBr_2(NO_2)_2+K_2SO_4+N+NO+CO_2+H_2O$. Potassium chlorodinitromethane behaves analogously. For the purposes of preparation, the direct action of halogens gives better yields than that of acids. Copper, lead, and ferrous salts have a similar action to that of mineral acids, but the silver monohalogenodinitromethanes can be obtained as stable, crystalline substances.

Dichloronitromethane is best prepared by the action of strong nitric acid on 2 : 4-dichloroacetanilide, and purified by conversion into the potassium salt, from which it is regenerated by the action of aqueous chlorine; it is a colourless oil, d_4^{25} 1·6616, not solidifying above −10°. Dibromodinitromethane, similarly purified, is a colourless, pungent oil, d_4^{25} 2·3946, m. p. 7·4°. *Potassium chlorodinitromethane*, light yellow prisms exploding at 83—85°, decomposes on keeping. *Silver chlorodinitromethane*, long, yellow needles, explodes at 80—81°. Chlorobromodinitromethane is best prepared in presence of sodium acetate, and forms a colourless, pungent liquid, d_4^{25} 2·0472. *Potassium iododinitromethane*, obtained by the action of iodine on potassium dinitromethane in aqueous solution, forms orange-yellow plates, exploding at 154°. It does not darken on exposure when pure. The *silver* salt forms insoluble, pale yellow, glistening leaflets, exploding at 109—110°. F. G. W.

Aliphatic Nitro-alcohols. II. R. WILKENDORF and M. TRÉNEL (*Ber.*, 1924, 57, [*B*], 306—309).—An extension of previous work (A., 1923, i, 288).

β-Chloro-β-nitroethyl alcohol condenses with acetaldehyde in aqueous solution, in the presence of a little potassium carbonate, to form *β-chloro-β-nitrobutane-αγ-diol*, $OH·CH_2·CCl(NO_2)·CH(OH)·CH_3$, long needles, m. p. 104°; with propaldehyde, it gives *β-chloro-β-nitropentane-αγ-diol*, colourless needles, m. p. 107° (decomp.). It does not appear to react with higher aldehydes.

The sodium derivative of β-chloro-β-nitroethyl alcohol is converted by methyl iodide in methyl-alcoholic solution into *β-chloro-β-nitropropyl alcohol*, m. p. 114°.

ment with a mixture of nitric acid (d 1·4) and concentrated sulphuric acid into β-*chloro*-β-*nitroethyl nitrate*, a colourless liquid, d^{18} 1·568, which, when cautiously heated, decomposes into nitric acid and α-*chloro*-α-*nitroethylene*, a liquid, b. p. 54—55°/14 mm., which violently attacks the eyes; the latter substance can also be prepared by the action of phosphoric oxide on β-chloro-β-nitroethyl alcohol; in the presence of sodium hydrogen carbonate, it passes readily into a *polymeride*, m. p. 126—130° (decomp.), according to the manner of heating. H. W.

Preparation of Ethyl Ether by Williamson's Method. W. B. S. Bishop (*J. Soc. Chem. Ind.*, 1924, **43**, 23—24T).—Pure ethyl ether is obtained readily by Williamson's method, using ethyl iodide and sodium ethoxide. The yield is 80% of the theoretical (calculated on the ethyl iodide used). The oxidised copper gauze test for halogens is capable of detecting as little as 0·00004 g. of iodine present as ethyl iodide in 1 c.c. of ether. W. P. S.

Catalytic Dehydration of Ethyl Alcohol and Ether by Alumina. R. N. Pease and C. C. Yung (*J. Amer. Chem. Soc.*, 1924, **46**, 390—403).—The dehydrations were carried out in an electrically heated glass bulb of 35 c.c. capacity containing the alumina. The alcohol was run in from a burette at a uniform rate, and, when equilibrium conditions had been obtained, a test was made. It is found that appreciable quantities of ether as well as ethylene are formed from alcohol and that at 275° and 300° the amount of alcohol decomposed attains a maximum corresponding with about 65% conversion, whereas at 350° the reaction proceeds to complete dehydration with the production of ethylene. The maximum yield of ether was 60% at 250°. Ether decomposes readily at temperatures above 275°. The results are explicable on the theory that the dehydration of alcohol to ether is a reversible equilibrium corresponding with about 65% conversion, and that decomposition of the alcohol occurs in steps. Whilst the direct dehydration to yield ethylene is a possible mechanism, it is not necessary to assume it in order to account for the results. Water vapour and ethylene diminish somewhat the efficiency of the catalyst towards dehydration of alcohol. Alumina which has been used in the dehydration of ether appears to be peculiarly activated with respect to alcohol, and the yield of ethylene is nearly doubled. A. B. S.

Autoxidation of Ethers. A. M. Clover (*J. Amer. Chem. Soc.*, 1924, **46**, 419—430).—The oxidising properties acquired by ethyl ether when exposed to the air (A., 1922, i, 619) have been observed with several other ethers. In three cases, the ether peroxides have been obtained, whereas in the other cases, owing to the high boiling point of the ether, the peroxides could not be isolated. Aldehydes, esters, acids, and hydrogen peroxide were also formed. The hydrolysis of the peroxides, which yields acids, hydrogen peroxide, and aldehydes, is considered to occur in accordance with the schemes: $OR{\cdot}CHR'{\cdot}O{\cdot}OH + H_2O \rightarrow R'CHO + ROH + H_2O_2$ or $OR{\cdot}CHR'{\cdot}O{\cdot}OH \rightarrow R'CO_2H + ROH$ or $R'CO_2R + H_2O$. The ethers experimented with were: propyl ether; *iso*propyl ether; *n*-butyl ether; *iso*amyl ether, b. p. 168—171°; methylenediethyl ether, b. p. 86—89°; benzylmethyl ether, benzylethyl ether, b. p. 183—185°; dibenzyl ether. In the case of propyl, *n*-butyl, and methylenediethyl ethers, the *peroxides* were isolated and analysed.

A. B. S.

Sulphochromic Oxidation and β-Oxidation. M. POLONOVSKI (*Compt. rend.*, 1924, **178**, 576—578).—A study of the oxidation of aliphatic acids by means of dilute sulphuric acid–dichromate solutions at 100°. Acetic acid is unaffected. Propionic acid is oxidised slowly and incompletely, through pyruvic and acetic acids (α-oxidation). Butyric acid is oxidised rapidly, through acetoacetic acid (β-oxidation; α-oxidation is shown not to occur from a consideration of the oxidation–time curves). Valeric acid undergoes β-oxidation, which in this case produces propionic acid, oxidation decelerating as a result.

E. E. T.

Electrolysis of Potassium Oleate. G. W. F. HOLROYD and J. E. W. RHODES (*J. Chem. Soc.*, 1924, **125**, 438—442).—The apparent transport number of the oleic-ion in $0{\cdot}2N$-potassium oleate solution was found to be 0·725, in agreement with that obtained by McBain and Bowden (T., 1923, **123**, 2417) under different experimental conditions. Oleic acid is the chief product at the anode; neither oxygen nor oxidation products in amount demanded by the equation, $2R{\cdot}CO_2 + H_2O = 2R{\cdot}CO_2H + O$, were found. The apparatus used was a modification of Ostwald's, arranged to allow collection of gases evolved.

F. G. W.

Bromine Derivatives of α-Elæostearic Acid. M. ISHIO (*J. Pharm. Soc. Japan*, 1923, No. 501, 789—796; cf. T., 1903, **83**, 1042; 1912, **101**, 2082; Nicolet, A., 1921, i, 390).—Dibromo-α-elæostearic acid (73 g.), colourless plates, m. p. 91°, is prepared by adding bromine to a solution of α-elæostearic acid (150 g.) in ether or light petroleum cooled below −15°; if chloroform is used as solvent, a tetrabromide (35 g.), m. p. 115°, is produced from the acid (100 g.) or from the dibromide. The dibromide is changed by alcoholic potassium hydroxide solution into a viscous oil free from the halogen, the reduction of which with hydrogen in the presence of platinum black yields stearic acid. When the tetrabromide is treated with alcoholic potassium hydroxide, a dibromide, $C_{18}H_{30}O_2Br_2$ or $C_{18}H_{32}O_2Br_2$, lustrous crystals, m. p. 40—40·5°, is produced.

K. K.

Perilla Oil. III. Bromides of the Linolenic Acids of Perilla Oil. K. H. BAUER (*Chem. Umschau*, 1924, **31**, 83—86; cf. A., 1923, i, 180).—Considerable quantities of linolenic acid hexabromides, prepared from perilla oil, were debrominated with zinc and alcohol and the linolenic acid obtained was brominated again. The precipitated bromides were separated. The soluble bromides were then debrominated and the separated fatty acids submitted to oxidation by Hazura's method. The solid oxidation products were mixed with sand and extracted in succession with boiling ether, light petroleum, and alcohol. From the alcoholic extract a small quantity of an acid, m. p. 143—147°, was obtained. The aqueous solution of the soluble oxidation products yielded a small quantity of a yellowish-brown oil and linusic acid, m. p. 203°. *iso*Linusic acid was not found. The hexabromides obtained from perilla oil were satisfactorily recrystallised from boiling xylene, whereby hexabromostearic acid, m. p. 179—181°, was isolated. All attempts to separate the product into components by fractional crystallisation of large quantities were without effect, so that the substance is presumably homogeneous. Owing to the uncertainty surrounding the oxidation of and formation of additive compounds from these highly unsaturated substances, it is not considered safe to assume that, because linusic acid is the only hydroxy acid obtained from the soluble brominated linolenic acids, the oxidation of β-linolenic acid yields this acid only. Attempts to prepare hexahydroxystearic acids from hexabromostearic acids by treating them with silver oxide were unsuccessful. The effect of allowing perilla oil to remain for a long time in the dark in contact with a small quantity of iodine (conditions favourable to the transformation of α- into β-elæostearic acid in the case of tung oil) was studied; steric rearrangement did not occur under the conditions chosen.

H. C. R.

Glycerides of Lard. II. Synthetical. C. Amberger and A. Wiesehahn [and, in part, J. Bauch] (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 291—299).—α-Oleo-βγ-distearin [glyceryl α-oleate βγ-distearate], m. p. 42°, was synthesised by Fischer and Pfähler's method (A., 1920, i, 807) from α-mono-olein and stearyl chloride. α-Palmito-αβ-diolein, synthesised in a similar manner from α-monopalmitin and oleyl chloride, is a dark yellow oil which solidifies at 0°. Attempts to synthesise oleopalmitostearin were unsuccessful. A comparison of the properties of the mixed glycerides isolated from lard with those synthesised (cf. A., 1922, i, 804) and those obtained by their hydrogenation, leads to the conclusion that the following are present: β-palmito-αγ-distearin, β-stearo-αγ-dipalmitin, α-oleo-αβ-distearin, α-palmito-αβ-diolein, and probably β-oleo-α-palmito-γ-stearin.

H. C. R.

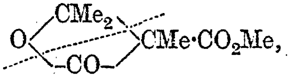
Crystalline Bromides of Linseed Oil. H. Toms (*Analyst*, 1924, **49**, 77—81).—A substance, m. p. 153° (corr.), is obtained by successive treatment of the crude bromide from linseed oil with ethyl acetate, alcohol, and ether. Its analysis agrees closely with the formula, $C_{57}H_{94}O_6Br_{16}$, from which it is concluded that it is a linolic–dilinolenic bromoglyceride. Its solubility in ethyl acetate at 15—20° is 0·15—0·20 g. per 100 c.c. The residue obtained from the ethyl acetate mother-liquor yields a small amount of material, m. p. 117° (corr.). The analysis of this substance corresponds approximately with the formula, $C_{57}H_{98}O_6Br_{12}$, and it may be trilinolic bromoglyceride or an oleic–linolic–linolenic bromoglyceride. Attempts were made to determine the bromide which was insoluble in ethyl acetate, and there were indications that the amount of the most unsaturated glyceride in linseed oil is a constant proportion of the total unsaturated substances present. H. C. R.

Uncommon Animal Fats. W. N. Rae (*Analyst*, 1924, **49**, 83—84).—The analytical characters of the fats of the following wild animals of Ceylon are given: leopard (*Felis pardus*), sambhur (*Cervus unicor*), spotted deer (*C. axis*), peafowl (*Pavo cristatus*), and wild boar (*Sus cristatus*). The values for leopard's fat agree closely with those given by Lewkowitsch for tiger's fat, and the values for the two members of the deer tribe agree with those of the chamois. European wild boar fat, however, differs considerably from that of the Ceylon wild boar. [Cf. *B.*, 1924, 264.] H. C. R.

β-Lactones of β-Hydroxybutyric Acid and its Alkyl Derivatives and the Influence of Constitution on the Decomposition of β-Lactones. H. Salkowski, jun. (*J. pr. Chem.*, 1923, **106**, 253—265).—When α-dialkylated β-hydroxybutyric acids are distilled they decompose into acetaldehyde and a dialkylacetic acid. A somewhat similar reaction to this is the thermal decomposition of methyl β-hydroxy-α-methyl*iso*propylmalonolactone, $O<\substack{CMe_2\\ CO}>CMe\cdot CO_2Me$, into acetone, dimethylketen, and carbon dioxide. To determine whether the decomposition of the β-hydroxybutyric acid may be preceded by the intermediary formation of a β-lactone which then decomposes into aldehyde and keten, the latter subsequently taking up the elements of water, β-lactones of β-hydroxybutyric acid, β-hydroxy-α-ethyl- and β-hydroxy-αα-dimethyl-butyric acids, were prepared and their thermal decomposition was studied.

The required hydroxybutyric acid derivatives were prepared by reduction of the corresponding derivatives of ethyl acetoacetate with sodium amalgam. β-*Hydroxy-α-ethylbutyric acid* is a viscous liquid, b. p. 123°/0·8 mm. β-*Hydroxy-αα-dimethylbutyric acid* forms a viscous liquid, b. p. 108—110°/0·02 mm., which slowly crystallises to bunches of needles, m. p. 34°. Part of the acid is converted into an *anhydride*, $OH\cdot CHMe\cdot CMe_2\cdot CO\cdot O\cdot CHMe\cdot CMe_2\cdot CO_2H$, b. p. 200—203°/15 mm., a very viscous liquid. The β-hydroxy-acids were converted into β-bromo-acids. For this purpose β-hydroxybutyric acid and β-hydroxy-α-ethylbutyric acid had first to be converted by distillation into the corresponding crotonic acid and the product treated with liquid hydrogen bromide. β-*Bromo-α-ethylbutyric acid* is a yellow, viscous liquid, b. p. 140—143°/15—16 mm.; β-*bromo-αα-dimethylbutyric acid* forms brown needles, m. p. 42°, b. p. 115°/0·2 mm. The lactones were obtained by treating the acids with sodium carbonate solution and extracting with ether. α-Ethyl-β-butyrolactone has b. p. 75°/13 mm. (cf. Johansson and Hagman, A., 1922, i, 426) and *αα-dimethyl-β-butyrolactone* has b. p. 63—65°/14 mm. The thermal decomposition of the lactones in each case gave carbon dioxide and an olefine, β-butyrolactone giving propylene, α-ethyl-β-butyrolactone giving amylene, and αα-dimethyl-β-butyrolactone giving α-methylbutylene. The decomposition is therefore different from that of the αα-dialkyl-β-hydroxybutyric acids.

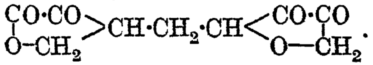
The type of β-lactone decomposition occurring in the case of methyl β-hydroxy-α-methyl*iso*propylmalonolactone,



$$O<\begin{array}{l}CMe_2\\ CO\end{array}>CMe\cdot CO_2Me,$$

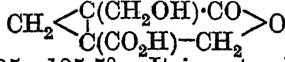
the so-called ketone-splitting, can probably only take place when the β-carbon atom is tertiary. E. H. R.

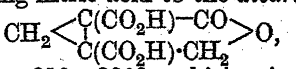
Condensation between Pyruvic Acid and Formaldehyde. Y. Asahina and S. Terada (*J. Pharm. Soc. Japan*, 1923, No. 502, 855—878).—The action of pyruvic acid on formaldehyde gives a compound, $C_9H_8O_6$, colourless plates, m. p. 239—240° (decomp.), which is shown to be methylenebis-α-ketobutyrolactone,



$$\begin{array}{l}CO\cdot CO\\ O{-}CH_2\end{array}>CH\cdot CH_2\cdot CH<\begin{array}{l}CO\cdot CO\\ O{-}CH_2\end{array}.$$

It gives the following derivatives: *ammonium* salt, $C_9H_7O_6\cdot NH_4$, white, silky crystals; *potassium* and *sodium* salts; unstable *silver* salt, $C_9H_6O_6Ag_2$, white scales; *ethyl* ester, m. p. 124—125°; monoacetyl derivative, scales, m. p. 135°; *dibenzoyl* compound, m. p. 122°; *phenylhydrazine* salt, $C_9H_8O_6,(Ph\cdot NH\cdot NH_2)_2$, white crystals, m. p. 195—196°; *phenylhydrazone*, $C_9H_8O_4(N\cdot NH\cdot Ph)_2$, m. p. 225—227° (decomp.); *semicarbazide* compounds, m. p. 196—197° (decomp.), and m. p. 182—183° (decomp.), respectively; *chloro-compounds*, m. p. 151—152°, and m. p. 183—184°. When heated at 145° with concentrated sulphuric acid, it yields an anhydride, $C_9H_6O_5$, white crystals, which do not melt below 300°.

Methylenebis-α-ketobutyrolactone is oxidised by silver oxide to the *substance*,  $CH_2<\begin{array}{l}C(CH_2OH)\cdot CO\\ C(CO_2H){-}CH_2\end{array}>O$, colourless, hexagonal crystals, m. p. 185—185·5°. It is not coloured by ferric chloride, but gives the pine-shaving reaction and contains one carboxy group, one lactone ring, and one hydroxy group. It yields a *methyl* ester, silky crystals, m. p. 105—105·5°, a *monoacetyl* derivative, m. p. 130°, and *monobenzoyl* compound, m. p. 130—131°. When heated with hydriodic acid and red phosphorus, it gives two iodine *compounds*, $C_7H_{10}O_4I_2$, m. p. 168—169° and 143—144°, respectively. When reduced with sodium amalgam, the former iodine compound gives *cis*-αγ-dimethylglutaric acid and the other the *trans*-isomeride. It is oxidised by fuming nitric acid to the *dicarboxylic acid*,



$$CH_2<\begin{array}{l}C(CO_2H){-}CO\\ C(CO_2H)\cdot CH_2\end{array}>O,$$

white crystals, m. p. 219—220°, which gives the pine-shaving reaction and contains two carboxyl groups and one lactone ring. Its *dimethyl* ester, prisms, melts at 77·5—78·5°. By heating with hydriodic acid and red phosphorus, it gives an iodine *compound*,

$C_6H_8O_4I_2$, m. p. 167—168°, the reduction of which with sodium amalgam produces αα-dimethylsuccinic acid. The similarity between the relation of β-tetronic acid to methylenebis-β-tetronic acid and that of α-tetronic acid to methylenebis-α-ketobutyrolactone was observed spectrographically. K. K.

Influence of Strong Acids on the Solubility of Oxalic Acid. W. Herz and E. Neukirch (*Z. anorg. Chem.*, 1923, **131**, 303—309).—The solubility of oxalic acid is depressed by the addition of a strong acid (hydrochloric, sulphuric, nitric) up to a certain concentration of the latter, after which it is increased. No action could be detected between oxalic and sulphuric acids up to a 3·5-molar concentration of the latter. Nitric acid exerts an oxidising effect, apparently due to impurities, and the figures obtained with this acid are not accurate. The results obtained are compared with those calculated on the solubility-product principle, the agreement being fair except in the case of nitric acid. [Cf. *B.*, 1924, 277.] S. K. T.

Photochemical Sensitisation of the Maleic Ester Transformation by means of Bromine. J. Eggert [with W. Borinski] (*Physikal. Z.*, 1924, **25**, 19—21).—A study of the transformation of maleic ester in carbon tetrachloride solution, in presence of bromine, into fumaric ether, under the influence of energy of wave-lengths 557, 436, and 365 μμ, gave the following results :—(1) The photochemical efficiency at 18° with blue light (436 μμ) is 565, much greater than the figure calculated from the equivalent law. (2) The transformation is proportional to the number of absorbed quanta, but independent of the concentrations of bromine and solvent within wide limits; it is proportional to the quantum dimension at uniform temperatures, and increases for the same radiated energy exponentially with the temperature. These results appear contradictory, and seem to indicate that the activated molecule can survive several collisions. S. I. L.

Correlation of Additive Reactions with Tautomeric Change. II. Reversibility in Relation to the Stability of Carbon Chains. E. H. Ingold (Usherwood) (*J. Chem. Soc.*, 1924, **125**, 435—438).—Failure to obtain a homologue by the method which leads to the formation of the parent substance may be due to the structure of the homologue admitting of some retrograde additive reaction by which it can break down. The influence of homology on the reversibility of such addition reactions thus becomes the determining factor in the ability to exist of various types of carbon structure.

The influence of homology on the reversibility of the aldol addition process is very marked. Thus in the cases of acetaldehyde, *iso*butaldehyde, and α-methylbutaldehyde, the percentages of aldol present in the equilibrium mixtures at 25° and 62° are, respectively, 100, 92 and 39, and 41 and 9. The failure of Neustädter (A., 1907, i, 14) to obtain α-methylbutaldehyde must be ascribed to the experimental limitations imposed on the aldol reaction by the influence of temperature and structure on its reversibility. In the case of acetaldehyde, reversibility could not be detected at the ordinary temperature, and experiments at 60° were rendered impossible by the formation of crotonaldehyde.

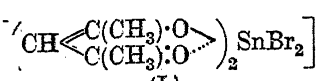
The position of the equilibrium, in the case of α-methylbutaldehyde, was determined by keeping the aldehyde or aldol, mixed with an equal volume of saturated aqueous potassium carbonate, in a closed vessel at a known temperature for a definite time, and working up as previously described (T., 1923, **123**, 1723), except that the distillation was finished at 125° in an atmosphere of carbon dioxide. *α-Methylbutaldol* forms a rather viscous, colourless liquid, b. p. 103—104°/6 mm., with a characteristic earthy odour.

F. G. W.

Dichloroacetaldoxime. O. ROUTALA and W. NEVVIUS (*Ber.*, 1924, **57**, [*B*], 252—254).—*Dichloroacetaldoxime*, $CHCl_2\cdot CH\!:\!N\cdot OH$, a colourless liquid with a penetrating odour, b. p. 67—69°/17 mm., 40—44°/2—3 mm. (partial decomp.), is prepared by the action of hydroxylamine hydrochloride on crude dichloroacetaldehyde obtained from trichlorolactic acid. It is converted by hydroxylamine at the atmospheric temperature into glyoxime. With phenylcarbimide, it yields the *compound*, $C_9H_8O_2N_2Cl_2,C_6H_6$, which darkens at 155° but has not a definite m. p. Attempts to transform it into the monoxime of glyoxal were not successful. H. W.

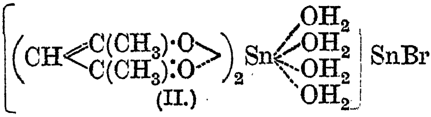
Condensation Products of Diethyl Ketone. J. B. EKELEY and M. S. CARPENTER (*J. Amer. Chem. Soc.*, 1924, **46**, 446—450; cf. Ekeley and Howe, A., 1923, i, 997).—The protracted action of an excess of diethyl ketone on sodium ethoxide at 10° leads to the production of a mixture of *homomesityl oxide* [*γ-ethyl-δ-methyl-Δ^γ-heptene-ε-one*], $CEt_2\!:\!CMe\cdot COEt$, and *homo*iso*phorone*, $C_{15}H_{28}O$. The former substance is a colourless liquid with a strong, mint-like odour and taste, b. p. 98—102°/20 mm., d_4^{20} 0·8535, n_D^{20} 1·4501. Homo*iso*phorone is a pale yellow, slightly viscous liquid, b. p. 137—140°/8 mm., d_4^{20} 0·91456, n_D^{20} 1·4831. A. B. S.

Residual Affinity and Co-ordination. XVII. Stannic Derivatives of β-Diketones. G. T. MORGAN and H. D. K. DREW (*J. Chem. Soc.*, 1924, **125**, 372—381).—The product of the reaction between molecular proportions of stannic chloride and acetylacetone in chloroform solution is a white, crystalline precipitate, m. p. 150° (decomp.), which deliquesces rapidly in air with formation of a crystalline substance, m. p. 98°. If instead of isolating this product, the reaction mixture is boiled with a second molecular proportion of acetylacetone, stannic bisacetylacetone dichloride, m. p. 202—203°, is obtained. This substance, contrary to Dilthey's statement (A., 1906, i, 342), is soluble in hot benzene, and its molecular weight in that solvent corresponds with the monomeric formula, $Sn(C_5H_7O_2)_2Cl_2$. The corresponding dibromide, obtained by the interaction of stannic bromide and copper acetylacetone in chloroform solution, does not react with stannic bromide when the two substances are dissolved together in anhydrous solvents, but the introduction of water leads to the formation of tetra-aquostannic bisacetylacetone stannibromide, $[(H_2O)_4Sn(C_5H_7O_2)_2]SnBr_6$. Stannic bisacetylacetone dibromide (I) and the tetra-aquo compound (II) exhibit co-ordination numbers of six and eight, respectively.



$$\left[\left(CH\!<\!\begin{matrix}C(CH_3)\cdot O\\ C(CH_3):O\end{matrix}\!>\right)_2 SnBr_2\right]$$

(I.)



$$\left[\left(CH\!<\!\begin{matrix}C(CH_3)\cdot O\\ C(CH_3):O\end{matrix}\!>\right)_2 Sn\!\begin{matrix}OH_2\\ OH_2\\ OH_2\\ OH_2\end{matrix}\right] SnBr_6$$

(II.)

The formation of stannic bis-β-diketone dibromides is a general reaction between stannic bromide and the copper salts of the β-diketones in chloroform, and proceeds according to the following equations: $3SnBr_4+3Cu\overline{Ac}_2=3Sn\overline{Ac}_2Br_2+3CuBr_2$; $3CuBr_2+Cu\overline{Ac}_2=2Cu_2Br_2+2\overline{Ac}Br$, where $\overline{Ac}$ is the univalent β-ketonic chelate group and $\overline{Ac}Br$ the corresponding bromo-β-diketone. The *cis-trans* (octahedral) isomerism theoretically possible has not yet been detected among these co-ordination compounds.

Stannic bisacetylacetone dibromide, transparent, colourless, lustrous, six-sided prisms, or aggregates of flaky crystals, m. p. 187°, separates from benzene as the double compound $[SnBr_2(C_5H_7O_2)_2]_2,C_6H_6$, which loses the solvent at 70—110°. *Tetra-aquostannic bisacetylacetone stannibromide*, obtained as described above or by the interaction of stannic bromide and stannic *bis*acetylacetone dibromide in presence of moisture, forms large, transparent, colourless prisms, m. p. 105—107°. When boiled with benzene, it loses water and dissociates into stannic bromide and the bisacetylacetone dibromide. *Stannic bisbenzoylacetone dibromide* is a white, microcrystalline powder, m. p. 213—214°, soluble in hot acetylacetone, with which it reacts to form benzoylacetone and the *bis*acetylacetone dibromide. 3-*Bromobenzoylacetone* was isolated as colourless prisms with an aromatic lachrymatory odour, m. p. 43—45°. *Stannic bisdibenzoylmethane dibromide*, shining, sulphur-yellow crystals, m. p. 276—278°, is only slowly hydrolysed by aqueous potassium hydroxide (40%) with formation of acetophenone. *Stannic bis-3-ethylacetylacetone dibromide*, transparent, colourless, six-sided prisms, m. p. 164—166° after softening at 162°, and 3-*bromo-3-ethylacetylacetone*, a pale yellow, lachrymatory liquid, b. p. about 195°, are described. F. G. W.

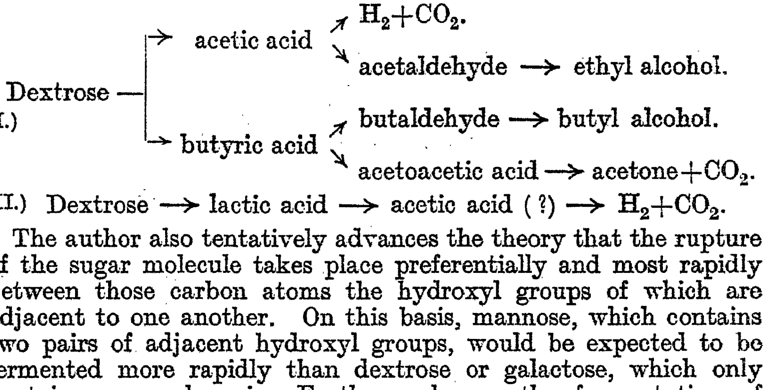
The α- and β-Forms of certain Monosaccharides. O. SVANBERG and K. O. JOSEPHSON (*Ber.*, 1924, **57**, [*B*], 297—299).—It is proposed to discriminate between the α- and β-forms of monosaccharides by observation of their differing affinity towards invertase. In the cases of dextrose and xylose, a distinct difference is observed in the behaviour of the two forms of the sugar; the α-variety of one sugar resembles exactly the β-variety of the other.

Amongst the monosaccharides, certain instances are encountered in which the more strongly dextro-rotatory variety (the α-form according to Hudson) can only be converted slowly, if at all, into the corresponding acetone-sugar, whereas in others (pentoses) the α-variety readily undergoes this change. When the α-sugar is very inert, the β-sugar is highly active.

The conclusions based on the two methods are identical in the cases of dextrose and xylose, but the available experimental data are insufficient to permit an extended proposal for the designation of α- and β-forms. H. W.

Molecular Configuration in the Sugars and Acid Production by *Bacillus Granulobacter Pectinovorum*. H. B. Speakman (*J. Biol. Chem.*, 1923, **58**, 395—413).—The non-volatile acid produced during the fermentation of starch by *Bacillus granulobacter pectinovorum* (cf. Reilly, Hickinbottom, Henley, and Thaysen, A., 1920, i, 465) has been identified as lactic acid, and the rates of formation of this acid, as well as those of acetic and butyric acids, during the fermentation of starch, arabinose, xylose, dextrose, galactose, and mannitol have been studied. From the results obtained, the fermentation of dextrose is provisionally regarded as taking place in two ways, according to the following schemes (cf. also A., 1920, i, 797):

(I.)


Dextrose
acetic acid
H_2+CO_2.
acetaldehyde → ethyl alcohol.
butyric acid
butaldehyde → butyl alcohol.
acetoacetic acid → acetone+CO_2.

(II.) Dextrose → lactic acid → acetic acid (?) → H_2+CO_2.

The author also tentatively advances the theory that the rupture of the sugar molecule takes place preferentially and most rapidly between those carbon atoms the hydroxyl groups of which are adjacent to one another. On this basis, mannose, which contains two pairs of adjacent hydroxyl groups, would be expected to be fermented more rapidly than dextrose or galactose, which only contain one such pair. Further, whereas the fermentation of dextrose should proceed mainly according to scheme (I), that of galactose should proceed mainly according to scheme (II). These deductions appear to be confirmed by experiment. Similar deductions from the configurations of the pentoses are also in accord with fact, but the theory appears to fail with respect to dulcitol, which, unlike mannitol, is not fermented by the bacillus (cf. also Robinson, A., 1922, i, 971). E. S.

Relations between Rotatory Power and Structure in the Sugar Group. I. The Halogenoacyl and Nitroacyl Derivatives of the Aldose Sugars. C. S. Hudson (*J. Amer. Chem. Soc.*, 1924, **46**, 462—477).—Investigations have been carried out with a view to determine the probable structure and physical constants of the as yet undiscovered α-halogenoacetylglucoses and related sugars as a help to their syntheses.

The application of van't Hoff's hypothesis of additive optical superposition to the two forms of dextrose penta-acetate permits the calculation of the rotation of the acetylated basal chain which is common to both varieties. If this value is subtracted from the known rotation of acetylbromoglucose, the numerical value for the halogenated carbon atom can be deduced. An extension of this method of calculation to a series of halogenoacetyl- and nitroacetylglucoses shows that the rotation of the terminal asymmetric carbon atom in these compounds is approximately a constant quantity for the various aldoses. A comparison of the calculated and observed values for a series of halogenoacetyl sugars, such as bromo- and chloro-acetyldextrose, indicates that they are to be classified as α-forms instead of, as previously, β-varieties.

Van't Hoff's theory is applicable also to the glucosamines and to derivatives of deoxyglucose. Bromoglucodesose tribenzoate (Bergmann, Schotte, and Leschinsky, A., 1923, i, 653), is an α-derivative whereas deoxymethylglucoside tribenzoate prepared from it is a β-form. Toluene-*p*-sulphonyltriacetylbromoglucose (Freudenberg and Ivers, A., 1922, i, 524) is also an α-variety, whereas the corresponding tetra-acetate and the methylglucoside belong to the β-series. A. B. S.

Relations between Rotatory Power and Structure in the Sugar Group. II. The Halogenoacetyl Derivatives of a Ketose Sugar [*d*-Fructose]. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1924, **46**, 477—483; cf. preceding abstract).—The theory of optical superposition may be applied to ketoses, the effect of the halogenated terminal carbon atom being of the same magnitude as for the aldoses.

In the case of the two isomeric lævulose penta-acetates, the calculated values for $[\alpha]_D$ are —5° and —103° in chloroform, whereas the observed rotations of the two known isomerides are $[\alpha]_D^{20}$ +34·7° and —121° in the same solvent. It seems very unlikely that the dextrorotatory form is the expected α-derivative; possibly it has a different ring structure from the compounds hitherto examined. The other isomeride, $[\alpha]_D^{20}$ —121°, may be the β-form, although a difference of 18° causes doubt; the fact that normal β-bromo- and fluoro-acetyl-lævuloses can be prepared from it are evidence in favour of the β-modification. A. B. S.

Relations between Rotatory Power and Structure in the Sugar Group. III. The Biose of Amygdalin [Gentiobiose] and its Configuration. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1924, **46**, 483—489).—The identity of the biose of amygdalin with gentiobiose is established by the observation that the rotation of the biose chain of amygdalin, as calculated from the rotations of two of its derivatives, *iso*amygdalin and prulaurasin, has the same value as the rotation of the chain of gentiobiose. The line of evidence is entirely independent of that of Haworth and Leitch (T., 1922, **121**, 1921) or Kuhn (A., 1923, i, 589). The combined results prove the configuration of gentiobiose to be that of 1 : 6-β-glucosidoglucose. Maltose and gentiobiose are the α- and β-glucos-

idic forms respectively of 1 : 6-glucosidoglucose; they constitute the first αβ pair of compound sugars to be definitely allocated.
A. B. S.

Polysaccharides. XXII. Lichenase and Reserve Cellulose [Lichenin]. XXIII. The Separation of Lichenase into Constituent Enzymes. P. KARRER and others.—(See i, 471.)

Polysaccharides. XXIV. The Occurrence of Lichenin (Reserve Cellulose) in Lichens and other Plants. P. KARRER, M. STAUB, and J. STAUB (*Helv. Chim. Acta*, 1924, 7, 159—162).—The preparation of lichenin is described from the lichens *Evernia vulpina*, *Usnea barbata*, L., and *Parmelia furfuracea*, Ach.; it is shown to be identical with that from Iceland moss, *Cetraria Islandica*. It also occurs in many other plants, such as barley, oats, maize, spinach, beans, hyacinth bulbs and others. [Cf. i, 471.]
E. H. R.

Starch Iodide. A. LOTTERMOSER (*Z. angew. Chem.*, 1924, **37**, 84—85; cf. this vol., i, 269).—The partition of iodine between starch, aqueous potassium iodide, and carbon tetrachloride was determined, using the partition coefficient of iodine between carbon tetrachloride and *N*/10-potassium iodide (=1·16 at 25°). The partition of iodine between carbon tetrachloride, aqueous potassium iodide, and soluble starch was also examined by the potentiometer method (cf. A., 1922, i, 10). The results agreed with those obtained by ultrafiltration of the starch iodide solution and analytical determination of the individual components before filtration and in the ultrafiltrate. Starch iodide is thus shown to be an adsorption product. The I_3-ion is most strongly adsorbed, the adsorption curve being normal. At the same time, the I-ion and undissociated KI and KI_3 are also adsorbed, whilst the expulsion of free iodine from the surface generally increases with increasing concentration. The determination of the partition of iodine between benzene, water, and starch (cf. von Euler and Myrbäck, A., 1922, i, 527, 1120) gave unsatisfactory results owing to the uncertainty of the partition coefficient of iodine between benzene and water. Analogous experiments using carbon tetrachloride in place of benzene give results in agreement with those quoted above, so that there is no evidence of chemical combination between the iodine and starch. Adsorbed iodine is given up again very incompletely by starch, so that the curves obtained by adjusting the equilibrium from "above" and "below" do not coincide. The actual adsorption equilibrium is, however, rapidly attained, but the starch continues to adsorb iodine owing, apparently, to a very gradual diffusion of the latter into it.
W. T. K. B.

Starch-Iodine Reaction. N. R. DHAR.—(See ii, 242.)

Topochemical Reactions. Esterification and Mercerisation of Cellulose. R. O. HERZOG and G. LONDBERG (*Ber.*, 1924, **57**, [*B*], 329—332).—Röntgen examination shows that the esterification of ramie fibre and a number of varieties of artificial silk is a normal, heterogeneous process which proceeds from exterior to interior accompanied by solution of the cellulose esters. The progress of the reaction does not depend on the degree of arrangement of the crystallites, but on the previous chemical and physical treatment of the material. The nitration of cellulose, on the other hand, is a typical topochemical reaction occurring in the swollen fibre as in a homogeneous chemical system; denitration of cellulose nitrate under mild conditions takes place similarly.

Röntgen photographs of ramie or hemp fibres which have been mercerised without tension by sodium hydroxide solution (about 17%) and subsequently washed until free from alkali, exhibit Debye-Scherrer rings in place of the original point diagrams, showing that the crystallites have taken all possible positions. When the fibre is mercerised under such tension that the length remains unchanged, however, a point diagram is subsequently obtained, showing that the crystals lie, as originally, with the same axis in the direction of the fibre, that the crystals of mercerised cellulose have the same axial ratio and angles as the crystals of the original cellulose, and that the molecule of mercerised cellulose differs but little from that of the original cellulose, possibly to such an extent as is involved by the displacement of an oxygen linking.

H. W.

Quantitative Determination of the Fluorescent Powers (the Spectro-fluorescometry) of Cellulose and its Derivatives. S. J. Lewis (*J. Soc. Dyers and Col.*, 1924, **40**, 29—40).—The work previously described (A., 1923, ii, 334) has been extended and the methods have been improved so that the investigation of the fluorescent powers of cellulosic substances is now claimed to be easily carried out and even capable of application to industrial problems. Particularly, the spark source of ultra-violet light has been replaced by a cooled rotating tungsten arc, whereby the original feebleness of the spectrum between λ 2750—3300 and λ 2640—2730 is avoided, the necessary time for exposure has been shortened, and the method is about one thousand times more efficient, the accuracy being within 1%.

The fluorescent powers of various classes of cellulosic substances such as pure papers, pure cellulose, hydrocellulose, oxycellulose, and cellulose acetate have been determined in reference to a new standard (a specially purified paper) and the type of fluorescent curve for each class has also been determined. The previous conclusion that the fluorescent power of a cellulosic substance is independent of its physical condition has been confirmed. For instance, the fluorescent curves of cellulose acetate powder, paper, and transparent film are very similar, and the fluorescent power of oxycellulose is almost independent of its method of preparation.

Numerous curves representing the fluorescent powers of cellulose and related substances are given and discussed.

A. J. H.

The Viscose Reaction. B. Rassow and M. Wadewitz (*J. pr. Chem.*, 1923, **106**, 266—332).—A study has been made of the factors affecting the viscosity of solutions of viscose (cellulose xanthate). By the action of sodium hydroxide solutions on cellulose there appears to be formed a definite compound, having the empirical composition $C_6H_{10}O_5,NaOH$. When solutions containing less than 35% of sodium hydroxide are used, there is an equilibrium set up between cellulose, sodium hydroxide, the compound, and water. The compound is slowly decomposed by absolute ethyl alcohol. The so-called ripening of cellulose xanthate solutions, during which a fall in viscosity takes place, is probably the result of two reactions, the gradual hydrolysis of the cellulose xanthate and the disruptive action of the sodium hydroxide present on the cellulose molecular aggregates. [Cf. *B.*, 1924, 289.]

E. H. R.

Lignin. I. Flax Lignin and some Derivatives. W. J. POWELL and H. WHITTAKER (*J. Chem. Soc.*, 1924, **125**, 357—364).—Flax lignin, obtained from flax shoves by digestion with 10% sodium hydroxide solution at 130°, can be purified to a homogeneous, light brown product of the composition

$$C_{40}H_{30}O_6(OH)_5(OMe)_4{\cdot}CHO,$$

by pouring its solution in aqueous acetone into a large volume of dilute hydrochloric acid. Its *acetyl* derivative,

$$C_{40}H_{30}O_6(OMe)_4(OAc)_5{\cdot}CHO,$$

a dark brown, amorphous solid, is insoluble in cold, dilute sodium hydroxide, but is readily hydrolysed by boiling with water, indicating that the acidic properties of the lignin are to be ascribed to phenolic hydroxyl groups. By the action of methyl sulphate under very mild conditions, three methoxyl groups can be introduced into the lignin molecule, forming *methyl-lignin*,

$$C_{40}H_{32}O_8(OMe)_7{\cdot}CHO,$$

which is insoluble in alkali hydroxide and very resistant to hydrolysis. Attempts to acetylate the methylated product were not successful, indicating some difference between the remaining hydroxyl groups in lignin and those in its derivatives. The product of the action of hydriodic acid on the lignin agrees closely in composition with a demethylated lignin, but it cannot be acetylated, showing that reduction accompanies the demethylation. Cold, concentrated nitric acid, or a mixture of nitric and sulphuric acids, converts the lignin into a *trinitro* derivative, $C_{42}H_{39}O_{22}N_3$, a red powder which contains one methoxyl group and behaves as an aromatic nitro compound; six acetyl groups can be introduced, forming *acetylnitrolignin.* At higher temperatures, nitration is accompanied by much oxidation. The lignin reacts energetically with chlorine and bromine in absence of sunlight, with evolution of halogen acid. The products, *chlorolignin* and *bromolignin*, $C_{40}H_{20}O_8Hal_2(OMe)_2(OH)_5{\cdot}CHO$, are soluble in alkali hydroxides, and have suffered partial demethylation. They are not affected by hot nitric acid, and are only partly dehalogenated by boiling with sodium hydroxide solution, indicating that the remaining halogen atoms are attached to aromatic nuclei. *Acetylchlorolignin*, $C_{53}H_{42}O_{21}Cl_{12}$, and *acetylbromolignin*, $C_{42}H_{30}O_{16}Br_{12}$, as well as the acetylnitrolignins, are readily hydrolysed. The presence of one aldehyde group in the lignin molecule is deduced from the action of Fehling's solution and of phenylhydrazine. Comparison of these results with those of Cross and Bevan, Klason (A., 1908, i, 707; 1923, i, 187), and Beckmann and Liesche (A., 1921, i, 546; 1922, i, 233), shows that the lignins from jute, flax, and pine are not identical, but that those from flax and winter rye straw are closely related.

On treatment of the neutralised washings from the lignin (see above) with calcium chloride solution, considerable quantities of the calcium salt of a substance resembling lignin, but having a much smaller methoxyl content, are obtained. From the solution of chlorolignin in cold alkali hydroxide, acids precipitate the *compound* $C_{43}H_{35}O_{16}Cl_6$. F. G. W.

Potash Fusion of Lignin, Cellulose, and Wood. E. HEUSER and F. HERRMANN (*Cellulosechem.*, 1924, **5**, 1—6).—The observations of Heuser and Winsvold (A., 1923, i, 541, 900) on the fusion of lignin are confirmed and extended. When iron powder is present the yield of aromatic products is increased and the elimination of carbon dioxide from the protocatechuic acid is promoted, but not to such a large extent as when the fusion is performed in an iron crucible; iron is dissolved. There is only a slightly lower yield when the fusion is carried out at 240—260° instead of 270—280°. In the presence of ammonium carbonate a portion of the pyrocatechol is re-converted into protocatechuic acid. Fusion in an atmosphere of carbon dioxide instead of hydrogen does not have this effect; an atmosphere of carbon dioxide exerts a protective influence in suppressing the formation of oxalic acid, but not so completely as hydrogen. Carbon dioxide also moderates the total reaction, presumably because it combines with the potassium hydroxide; more lignic acid remains in the product. Carbon dioxide is produced to the extent of 27—28% of the weight of lignin when the fusion is carried out in a nickel crucible in the presence of air. Since the decomposition of protocatechuic acid into pyrocatechol is only pronounced in the presence of a catalyst in an atmosphere of hydrogen, the carbon dioxide formed under normal conditions is the result of oxidation at the expense of a portion of the products of reaction. Pure pyrocatechol is substantially resistant under the conditions employed. The fusion of cellulose with potash yields no aromatic products, only oxalic acid, with 21—22% of acetic acid and 1·5—2% of formic acid. The amount of oxalic acid is not substantially altered by the use of an atmosphere of hydrogen or by adding iron as catalyst; thus its formation from cellulose is not a process of oxidation. The fusion of wood gives results exactly compatible with those described for lignin and cellulose. J. F. B.

Nature of Lignin. E. STRUPP (*Cellulosechem.*, 1924, **5**, 6—7.)—The cyclo-saccharides or cycloses may be regarded as intermediate links capable of uniting partly with true carbohydrates and partly directly with one another. The presence of hydroaromatic rings in lignin and its undetermined position between the aromatic and aliphatic systems are cited as arguments in favour of the investigation of this conception. The methyl ether of inositol is a constituent of the cambial sap of certain conifers, and from inositol are obtainable several of the aromatic and aliphatic derivatives which have been detected in the products of decomposition of lignin. J. F. B.

Transformation of Ligneous Plant Substances into Coal. I. Production of Coal-like Products from Cellulose. C. G. SCHWALBE and R. SCHEPP (*Ber.*, 1924, **57**, [*B*], 319—322).—Cellulose can be converted into coal-like substances by salts which are present in sea water at a relatively low temperature and with surprising rapidity.

Coal-like substances, the composition and nature of which have not been fully examined, are produced from wood tissue and concentrated magnesium chloride solution at 150—180°, 135°, and 95°, respectively; a similar effect is produced by zinc chloride but not by calcium chloride solutions at 135°. Since in every case hydrochloric acid is produced it remains uncertain whether the effect is to be ascribed to dehydration or to hydrolysis of cellulose to dextrose and carbonisation of the latter. H. W.

Synthesis of some New β-Amino-acids, Esters, and Alcohols. R. BRECKPOT (*Bull. Soc. chim. Belg.*, 1923, **32**, 412—433).—Using three alkyl-substituted β-aminobutyronitriles described by Bruylants (A., 1923, i, 762) as a starting-point, the author has effected their hydrolysis and the esterification of the resulting acids, and has studied the reduction of these esters and also their reactions with magnesium ethyl bromide. The following compounds are described: β-*Dimethylaminobutyric acid hydrochloride*, hygroscopic needles, obtained by the action of concentrated hydrochloric acid on β-dimethylaminobutyronitrile, *chloroplatinate*, small orange crystals, m. p. 194—195° (decomp.). *Ethyl* β-*dimethylaminobutyrate*, b. p. 69·5°/12 mm., 183·5—184·5°/758 mm. (partial decomp.), d_4^{20} 0·91958, n_D^{20} 1·42641, prepared by the action of dry hydrogen chloride on an alcoholic solution of the hydrochloride of the acid, when an oil, $C_9H_{17}O_4N$, b. p. 105—110°/12 mm., which could not be identified, was produced simultaneously. The ester yields a *methiodide*, colourless needles, m. p. 127—128°, and a *chloroplatinate*, flattened orange-red prisms, m. p. 178—179° (decomp.), whilst on reduction with sodium and absolute alcohol, β-*dimethylaminobutyl alcohol*, b. p. 178—180°/760 mm., d_4^{20} 0·896, n_D^{20} 1·4408, is obtained. (The hygroscopic *methiodide*, m. p. 262—263°, and the non-crystalline *hydrochloride* are described.) The ester on treatment with magnesium ethyl bromide yields a mixture of diethylpropylenecarbinol, $CHMe{:}CH{\cdot}C(OH)Et_2$, and *αα-diethyl-γ-dimethylaminobutan-α-ol*, b. p. 205—212°, d_4^{20} 0·873, n_D^{20} 1·4410 (*methiodide*, m. p. 140—142°, *hydrochloride*, a white, extremely hygroscopic solid). β-*Ethylaminobutyric acid hydrochloride*, a crystalline mass, m. p. 72—73°, was also prepared by the action of hydrochloric acid on the corresponding nitrile; the corresponding free acid could not be prepared. *Ethyl β-ethylaminobutyrate*, b. p. 74°/12 mm., d_4^{20} 0·91549, n_D^{20} 1·42531 (*hydrochloride*, m. p. 111—114°), was obtained by passing dry hydrogen chloride through an alcoholic solution of the acid, with simultaneous production of a colourless oil, $C_{14}H_{27}O_6N$, b. p. 111—114°/19 mm. On reduction, the ester yields *β-ethylaminobutyl alcohol*, b. p. 187°, and is converted by treatment with magnesium ethyl bromide into the *lactam* of *β-ethylaminobutyric acid*, $CO<\begin{matrix}CH_2\\NEt\end{matrix}>CHMe$, b. p. 79·5—80·5°/12·5 mm., d_4^{20} 0·9420, n_D^{20} 1·4478 (*hydrochloride*, m. p. 72—73°); a theoretical explanation of its formation is given. At the same time, an octadiene, a colourless liquid, b. p. 127—130°/761 mm., and a small quantity of hygroscopic white needles, b. p. 255—265°, which were not identified, were produced. *Ethyl β-methylaminobutyrate*, b. p. 72°/12·5 mm., was prepared in a similar manner to its homologue; with magnesium ethyl bromide it yields the *lactam* of *β-methylaminobutyric acid*, b. p. 73—74°/12 mm., together with the same octadiene mentioned above.

The author points out that the three esters described may all be obtained from allyl bromide as a starting point (cf. Bruylants, A., 1922, i, 817), and the yields at each stage are good. H. J. E.

Salting-out of Amino-acids. P. Pfeiffer and O. Angern (*Z. physiol. Chem.*, 1924, **133**, 180—192).—*l*-Tyrosine, *l*-asparagine, *d*-glutamic acid, and glycylglycine are not salted out by ammonium sulphate and sodium acetate. Glycine and sarcosine are salted out to a greater or less degree by potassium acetate, *l*-cystine by ammonium sulphate, and *dl*-alanine by potassium acetate and ammonium sulphate. *l*-Leucine, *dl*-phenylalanine, and *l*-tryptophan are precipitated by sodium chloride, potassium acetate, and ammonium sulphate. S. S. Z.

Amino-acids and Polypeptides in Combination with Neutral Salts. IV. P. Pfeiffer, M. Klossmann, and O. Angern (*Z. physiol. Chem.*, 1924, **133**, 22—61).—Compounds of glycine, alanine, sarcosine, betaine, glycylglycine, alanylglycine, and di- and tri-glycylglycine, with a number of metallic salts, mainly alkali halides, were prepared and analysed. S. S. Z.

Oxidation of Amino-acids with Hydrogen Peroxide and at the Anode. F. Fichter and F. Kuhn (*Helv. Chim. Acta*, 1924, **7**, 167—172).—The oxidation of glycine in 2*N*-sulphuric acid solution, in presence of ferrous sulphate, with hydrogen peroxide proceeds partly according to the equation, $NH_2{\cdot}CH_2{\cdot}CO_2H+3O=NH_3+2CO_2+H_2O$, but only about half the theoretical quantity of ammonia and carbon dioxide can be accounted for. When insufficient hydrogen peroxide for the above equation is used, some formic acid is produced. When the oxidation is carried out in presence of ammonia, only minute amounts of carbamide are formed. By electrochemical oxidation of glycine in presence of ammonia, using ammonium nitrate as the electrolyte, larger quantities of carbamide are formed, and still larger quantities if ammonium carbonate is used instead of the glycine. It is concluded, therefore, that when glycine is used, the carbamide is formed from its decomposition products (cf. Fichter and Schmid, A., 1920, i, 824).

Oxidation of α-alanine with hydrogen peroxide in dilute sulphuric acid in presence of ferrous sulphate gives ammonia, acetaldehyde, acetic acid, formaldehyde, formic acid, and carbon dioxide; anodic oxidation in acid solution gives the same products. Anodic oxidation of leucine gives a mixture of *iso*valeraldehyde, *iso*valeric acid, *iso*butyric acid, acetone, acetic acid, formic acid, carbon dioxide, and ammonia. E. H. R.

Nitrogenous Components of Beetroot and Beetroot Products. E. O. von Lippmann (*Ber.*, 1924, **57**, [*B*], 256—258).—An account of experiments completed in 1902.

The following substances have been isolated from the solutions obtained after removal of sugar: *d*-arginine, m. p. 207°, $[\alpha]_D^{20}$ +11·25° in aqueous solution; *d*-lysine, m. p. 193·5°, $[\alpha]_D^{20}$ +15·42° when dissolved in water; *l*-histidine, m. p. above 280° (decomp.), $[\alpha]_D^{20}$ −39·48°; proline, m. p. 203°, $[\alpha]_D^{20}$ −3·12°; scatolecarboxylic acid, m. p. 162·5°; *l*-cystine, m. p. about 260° (decomp.), $[\alpha]_D^{20}$ +221° in hydrochloric acid solution (10%). The juice of freshly-harvested but still unripe beetroot yielded *l*-phenylalanine, m. p. 263°, a substance, $C_{18}H_{20}O_5N_2$, m. p. 275°, $[\alpha]_D^{20}$ +94·15° and +38·65° in faintly acidic and alkaline solution, respectively, which is probably identical with tyrosine anhydride (A., 1922, i, 184), and a substance, $C_6H_7O_4N$, colourless prisms, m. p. 125°, probably the imide of tricarballylic acid (cf. Thole and Thorpe, T., 1911, **99**, 1688). H. W.

Deamination of Esters of Alanine and Amino*iso*butyric Acid. A. L. Barker and G. S. Skinner (*J. Amer. Chem. Soc.*, 1924, **46**, 403—414).—*Ethyl α-amino*iso*butyrate hydrochloride*, m. p. 155—157° (corr.), is converted by a slight excess of sodium nitrite in aqueous solution at 0° into ethyl α-methylacrylate, ethyl α-hydroxy*iso*butyrate, and a little α-methylacrylic acid. Under similar conditions, methyl α-amino*iso*butyrate hydrochloride yields very small amounts of α-methoxy*iso*butyric acid which contains a small proportion of α-hydroxy*iso*butyric acid and α-methylacrylic acid together with methyl α-methylacrylate and methyl α-hydroxy*iso*butyrate. Methyl α-aminopropionate hydrochloride gives methyl acrylate, methyl α-chloropropionate, and methyl lactate, in addition to a non-volatile residue which is regarded as a pyrazolinedicarboxylic ester; the acidic products include α-methoxypropionic acid, lactic acid, and unsaturated and chloro acids. Ethyl α-aminopropionate hydrochloride yields ethyl acrylate, ethyl chloro- and hydroxy-propionates, ethyl diazopropionate, acrylic, lactic, α-chloropropionic, and α-ethoxypropionic acids, and certain nitrogenous residues which have not been identified. A. B. S.

Attempts to Prepare a Cyanide of Tin. J. G. F. Druce (*Chem. News*, 1924, **128**, 115—116).—No compound of tin with the cyanogen radical could be obtained by boiling an ethereal solution of stannous chloride with silver cyanide or ethyl cyanide. Freshly precipitated stannic hydroxide was dissolved in hot dilute hydrocyanic acid, and the filtered solution on evaporation in a vacuum left a pale brown, amorphous residue insoluble in water, alcohol, or ether. Analysis gave results closely agreeing with the formula $Sn(OH)_3{\cdot}CN$. Lead cyanide is produced by adding an excess of potassium cyanide to a saturated solution of lead nitrate; it is a white precipitate slightly soluble in hot 5% hydrocyanic acid, from which it crystallises in colourless needles. A. R. P.

Oxidation of Saturated Hydrocarbons by Ozone. R. Koetschau and W. Flemming (*Z. angew. Chem.*, 1924, **37**, 42—44).—Saturated cyclic hydrocarbons are attacked by ozone, as is shown by a marked increase in their viscosity and refractive index. The products obtained from decahydronaphthalene are mainly of the nature of peroxides which, unlike normal ozonides, dissolve in saturated hydrocarbons. When they are treated with water, hydrogen peroxide is formed, accompanied, not by aldehydic products, but by hydroxylic and carboxylic compounds. A small proportion of decahydronaphthol was identified in the reaction products, but the constitution of the peroxides and acids is still uncertain. The oxidation is far-reaching, and is complicated by the apparent partial rupture of the ring structure, with liberation of carbon dioxide. W. T. K. B.

Benzene and the Tetrahedron Formula. C. W. A. Lely (*Chem. Weekblad*, 1924, **21**, 114—117, 117—124).—Further arguments are quoted in support of the author's triangular formula (A., 1923, i, 99, 313, 767) and criticising the arguments brought against it by Olivier, van Roon, Schoutissen, and Derx and Hermans (*ibid.*, 195, 196, 451). The conclusion is drawn that the benzene formula of Kekulé and van't Hoff's tetrahedron conception of the carbon atom no longer serve to cover all the known facts. S. I. L.

Contact Condensation of Acetylene. N. Zelinsky.—(See i, 359.)

Hydrocarbons of Kerosene. C. R. Wagner.—(See i, 357.)

Action of Nitrogen Tetroxide on Aromatic Hydrocarbons, particularly Toluene. A. Schaarschmidt and E. Smolla (*Ber.*, 1924, **57**, [*B*], 32—42).—Nitrogen tetroxide scarcely reacts with cold benzene, more readily with toluene or xylene, immediately with mesitylene with evolution of heat. A study of the interaction of the tetroxide (1 part) and the hydrocarbon (3 parts) during extended periods at the atmospheric temperature, shows that benzene gives mainly nitrobenzene, picric acid, and some dinitrobenzene. *p*-Chlorotoluene is oxidised and nitrated to *p*-chlorobenzoic acid and nitro derivatives. Xylene and mesitylene are transformed into resinous products, oxidation occurring to a particularly marked degree in the case of mesitylene. Toluene is converted into oxalic acid (the yield of which increases greatly with prolongation of the action), benzoic acid, phenols, and benzaldehyde; the residue remaining after the product has been treated successively with water, sodium carbonate, sodium hydroxide, and sodium hydrogen sulphite consists mainly of almost equal proportions of unsaponifiable nitrotoluenes and readily hydrolysed nitrous or nitric esters of dinitrocresol. The unsaponifiable portion contains about 66% of mononitrotoluene; the remainder is a mixture of nitro products of higher boiling point, the least volatile of which decomposes explosively when heated in a vacuum at 200°. In the earlier stages of the reaction, acid, aldehydic, and neutral products are formed the weights of which are approximately in the ratio 3 : 2 : 4; when, however, the reaction is prolonged, the aldehydic components disappear almost completely in favour of the acid substances. The action depends greatly on the purity of the nitrogen tetroxide employed, and is most vigorous in the absence of water. H. W.

Reaction of Organo-Magnesium Compounds with Cupric Chloride. E. SAKELLARIOS and T. KYRIMIS (*Ber.*, 1924, **57**, [*B*], 322—326).—Diphenyl, 4 : 4′-ditolyl, 1 : 1′-dinaphthyl, and *s*-diphenylethane have been prepared by treating cupric chloride with the appropriate magnesium monoaryl halide (cf. Krizewsky and Turner, T., 1919, **115**, 559). Cupric chloride converts magnesium styryl bromide into $\alpha\delta$-diphenyl-$\Delta_{\alpha\gamma}$-butadiene, m. p. 147°, and magnesium *iso*amyl bromide into $\beta\eta$-dimethyloctane, b. p. 159—160°. Hydrodicamphene, m. p. 86°, is prepared from pinene hydrochloride. H. W.

Catalytic Effects of Zinc Chloride and Aluminium Chloride. J. F. NORRIS (*Ind. Eng. Chem.*, 1924, **16**, 184).—When the molecular compound of triphenylmethyl chloride and aluminium chloride is treated with ether, triphenylmethane is formed. This reaction is considered to proceed in the following way: $Ph_3C\cdot Cl+Et_2O=Ph_3C\cdot OEt+EtCl$; $Ph_3C\cdot OEt=Ph_3CH+MeCHO$. The first reaction is analogous to the action of aluminium chloride on a solution of benzoyl chloride in ether, the second reaction can be effected by heat alone, or in presence of aluminium chloride at the ordinary temperature. Triphenylmethane can therefore be prepared by allowing a mixture of carbon tetrachloride, benzene, and aluminium chloride to stand over-night; ether is then added, and after some hours the mixture decomposed with water. Excellent yields and a pure product are obtained. Primary alcohols are found to react readily with concentrated hydrogen chloride solution in presence of zinc chloride. This seems to indicate that the rôle of zinc chloride in reactions of this type is not that of a dehydrating agent, but of a catalyst operating by means of the formation of a molecular compound with the alcohol. C. I.

Hexaphenyl, the Linear Chain of Six Benzene Nuclei. R. PUMMERER and K. BITTNER (*Ber.*, 1924, **57**, [*B*], 84—88).—In continuation of previous work (A., 1922, i, 1196), 1-phenyl-

4-*p*-aminophenylbenzene is described in greater detail together with its transformation into hexaphenyl.

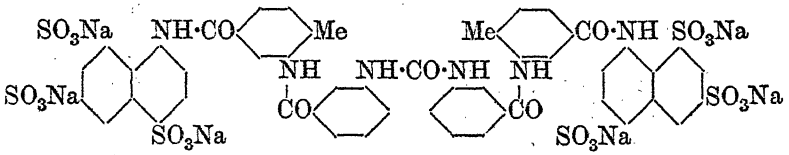
The preparation of 1-phenyl-4-*p*-aminophenylbenzene has been improved in many details; its success depends greatly on the purity of the reagents employed. 1-*Phenyl*-4-p-*acetamidophenylbenzene*, slender needles, m. p. 294°, 1-*phenyl*-4-p-*benzylideneaminophenylbenzene*, m. p. 262°, and the *compound*, $C_{28}H_{19}O_2N$, obtained from the base and *p*-naphthaquinone, are described. The amino compound yields a granular, yellow *diazonium sulphate* which is converted by potassium iodide into 1-*phenyl*-4-p-*iodophenylbenzene*, colourless leaflets, m. p. 247°. The action of silver powder on the iodo compound at about 330° leads to the production of *hexaphenyl*, $Ph{\cdot}[C_6H_4]_4{\cdot}Ph$, small, colourless, rhombic leaflets, m. p. 475°.

H. W.

Mechanism of the Reaction of *iso*Cyanates and *iso*Thiocyanates with the Grignard Reagent. H. Gilman and C. R. Kinney (*J. Amer. Chem. Soc.*, 1924, **46**, 493—497).—The reaction between phenyl *iso*cyanate and the Grignard reagent may be represented by the scheme : (I) PhN:C:O + PhMgBr → PhN(MgBr)·C(Ph):O → PhNH·C(Ph)O or (II) PhN:C:O+PhMgBr → PhN:C(Ph)OMgBr → PhN:C(Ph)OH, the last compound undergoing rearrangement to benzanilide. To decide between the two schemes, attempts were made to displace the MgBr in the additive compound by other radicals before hydrolysis. The introduction of methyl and ethyl groups was attempted, using methyl and ethyl sulphates, but the product obtained on hydrolysis was always benzanilide. The same occurred when diphenylmethyl chloride, triphenylmethyl chloride, methyl iodide, ethyl iodide, allyl bromide, and *p*-nitrobenzyl bromide were used. As the MgBr group is more easily replaced when attached to sulphur, the *iso*thiocyanates were investigated. When the Grignard compound was treated with methyl sulphate or ethyl sulphate, the products of hydrolysis were always *S*-methylthiobenzanilide and *S*-ethylthiobenzanilide, indicating that the addition of PhMgBr had taken place, not on the ·N:C:, but on the :C:S, group, the ·MgBr going to the sulphur. Scheme (II) represents the action in the case of the *iso*thiocyanates, and on account of the similarity of the *iso*cyanates, the same scheme probably represents the reaction in their case also.

A. B. S.

New Series of Trypanocidal Drugs. E. Fourneau, J. Tréfouël, (Mme.) J. Tréfouël, and J. Vallée (*Compt. rend.*, 1924, **178**, 675—676).—A substance (called 309) resembling Bayer 205 in all physical and trypanocidal properties, has been prepared. It is a grey or flesh-coloured powder, very soluble in water, insoluble in alcohol, and readily hydrolysed by concentrated sulphuric acid. Whilst 20-g. mice are completely unharmed by doses of 10—12 mg., mice infected with *Trypanosoma brucei* (Nagana) are cured by doses of 0·062 mg., infection of 2 days' standing being arrested by half this quantity. The drug is prepared as follows : sodium 1-naphthylamine-4 : 6 : 8-trisulphonate is condensed, in presence of sodium acetate, with 2-nitro-*p*-toluoyl chloride. The resulting nitro-compound is reduced, the amino compound obtained being condensed with *m*-nitrobenzoyl chloride. The product is reduced, and the amino compound formed condensed with carbonyl chloride. Bayer 205 (or the new compound, 309) is the sodium salt (following formula) of the resulting carbamide:

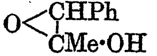
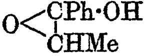


A large number of allied substances have been prepared, none of which has the physiological action of Bayer 205. The slightest constitutional change, *e.g.*, as obtained by using the above acid chlorides in the reverse order, is accompanied by complete suppression of trypanocidal action. E. E. T.

Compounds of the 2-Fluorenylmethyl Series. J. von Braun and H. Engel (*Ber.*, 1924, **57**, [*B*], 191—194; cf. A., 1923, i, 1087).—The cyano group of 2-cyanofluorene can be smoothly reduced to the methylamino group, without the occurrence of hydrogenation of the nucleus, by the action of hydrogen in the presence of nickel on a solution of the compound in decahydronaphthalene at 100°. 2-*Fluorenylmethylamine* and *di*-2-*fluorenylmethylamine* are thereby produced; they are separated from one another by taking advantage of the widely differing solubilities of the respective hydrochlorides in water. The primary base is a colourless, crystalline mass, m. p. 113°, b. p. 215°/10 mm.; the corresponding *hydrochloride*, m. p. 275—278° (decomp.), the *picrate*, m. p. 210°, the *acetyl* derivative, m. p. 171°, and the *phenylthiocarbamide* compound, colourless needles, m. p. 169°, are described. The secondary base, m. p. 147°, gives a *hydrochloride* which does not melt below 360° and a *nitroso* derivative, needles, m. p. 212°. Nitrous acid transforms the primary amine into 2-*fluorenylmethyl alcohol*, colourless crystals, m. p. 131°, which gives an intense bluish-green coloration with concentrated sulphuric acid; it is converted by the requisite phosphorus halide into 2-*fluorenylmethyl chloride*, m. p. 100°, and 2-*fluorenylmethyl bromide*, a pale yellow, crystalline mass, m. p. 95°. With trimethylamine, the bromide yields quantitatively 2-*fluorenylmethyltrimethylammonium bromide*, m. p. 218—219°, whilst when treated successively with hexamethylenetetramine and water, it is transformed into *fluorene*-2-*aldehyde*, colourless crystals, m. p. 174—175° (*semicarbazone*, m. p. 245—247°). 2-*Fluorenylacetonitrile*, m. p. 124°, is hydrolysed to 2-*fluorenylacetic acid*, m. p. 178°. H. W.

Kinetic Behaviour of Mixtures of Isomeric Nitrophenols on Reduction with Stannous Chloride. A. Klemenc (*Annalen*, 1924, **435**, 321—322).—The result obtained previously (this vol., i, 36) might have been due to the use of acid at only one concentration. The same result is now obtained varying this concentration, of which it is therefore independent. E. E. T.

Rôle of Weight of Acyl in the Migration from Nitrogen to Oxygen. L. C. Raiford and C. E. Greider (*J. Amer. Chem. Soc.*, 1924, **46**, 430—437; cf. Raiford, A., 1920, i, 156).—To investigate the influence of the weight of the acyl group on migration from nitrogen to oxygen, mixed diacyl derivatives of the three aminophenols were prepared, using the acetyl, benzoyl, and α-naphthoyl radicals. It is concluded that weight is the deciding factor and that migration is independent of substituents in the aminophenol nucleus. The heavier group is always found attached to nitrogen. o-α-*Naphthoylamidophenyl acetate* was obtained when *o*-acetamidophenol in pyridine solution was treated with the calculated quantity of naphthoyl chloride; it forms pink crystals, m. p. 133°. o-α-*Naphthoylamidophenol* is obtained when the acetate is allowed to stand in contact with a 1% solution of potassium hydroxide for 12 hours; very fine needles, m. p. 190°. The constitution of *o*-α-naphthoylamidophenyl acetate was proved by preparing *o*-α-naphthoylamidophenol from *o*-aminophenol and acetylating it, when the same substance was obtained. 5-*Bromo*-3-*naphthoylamido*-p-*tolyl acetate* was obtained from 5-bromo-3-acetamido-*p*-cresol by the same method as above; it crystallises in needles, m. p. 218°. 5-*Bromo*-3-*naphthoylamido*-p-*cresol* forms colourless needles, m. p. 151°. 4 : 6-*Dibromo*-2-α-*naphthoylamidophenyl acetate*, from 4 : 6-dibromo-2-acetamidophenol, crystallises in colourless needles, m. p. 226°. 4 : 6-Dibromo-2-α-naphthoylamidophenol, from the acetate by leaving it in contact with 2% alkali solution for 24 hours, crystallises in needles, m. p. 175°. It was also prepared by benzoylating 4 : 6-dibromo-2-aminophenol; the product was acetylated and identified with the acetate prepared as above. o-α-*Naphthoylamidophenyl benzoate* was obtained from *o*-benzoylamidophenol by the method described above, the yield being poor; it forms colourless needles, m. p. 176°. 4 : 6-*Dibromo*-2-α-*naphthoylamidophenyl benzoate*, from 4 : 6-dibromo-2-benzoylamidophenol, by the action of α-naphthoyl chloride, crystallises poorly, m. p. 235°. Its structure was proved by benzoylating 4 : 6-dibromo-2-α-naphthoylamidophenol, when the same substance was obtained. A. B. S.

Benzoylmethylcarbinol and Acetylphenylcarbinol. K. von Auwers and O. Jordan (*Biochem. Z.*, 1924, **144**, 31—43).—Benzoylmethylcarbinol has been prepared by the method of Auwers (A., 1918, i, 18), by hydrolysis of the acetyl compound with barium carbonate in water at 100°, and by hydrolysis of α-bromopropiophenone in aqueous alcohol solution with silver oxide. After purification by distillation in a vacuum, the refractive indices of the various preparations were measured, and these showed no alterations over a period of eight weeks. The purest preparation had n_D^{20} 1·5366, and was not affected by dilute acid or alkali nor by conversion to the acetyl compound and regeneration of the parent carbinol, which is therefore concluded to be a perfectly stable compound. The observations of Neuberg and Ohle (A., 1922, i, 480, 540) on the partial interchange of benzoylmethylcarbinol (α-ketol), Ph·CO·CH(OH)·CH_3, into acetylphenylcarbinol (β-ketol), OH·CHPh·COMe, also obtained biosynthetically by the action of the enzyme carboligase (A., 1921, i, 480), are therefore not confirmed. A mixture of these two compounds (α- and β-ketols) is obtained by the oxidation of α-phenylpropylene αβ-glycol (Zincke and Zahn, A., 1910, i, 316). Attempts to prepare acetylphenylcarbinol from methylbenzylcarbinol were unsuccessful, and the products obtained from phenylacetone (Carapelle, A., 1904, i, 158) consisted chiefly of derivatives of the α-ketol. The mechanism of this reaction is discussed. Finally, attempts to obtain acetylphenylcarbinol from methylbromobenzyl ketone by the action of silver oxide yielded a product (n_D^{20} 1·5152) to which the formula  $\mathrm{O}<\begin{array}{l}\mathrm{CHPh}\\ |\\ \mathrm{CMe{\cdot}OH}\end{array}$ or  $\mathrm{O}<\begin{array}{l}\mathrm{CPh{\cdot}OH}\\ |\\ \mathrm{CHMe}\end{array}$ is ascribed, on spectrochemical grounds, and since it does not react with semicarbazide. It is suggested that the slow change of refractive index observed by Neuberg and Ohle (*loc. cit.*) in their preparations may be due to the activity of spores normally present in a biochemical and absent from a chemical laboratory (cf. Auwers and Lange, A., 1922, i, 684).

J. P.

The Presence of the Resorcinol Nucleus in the Tannin of Quebracho Wood. M. NIERENSTEIN (*Ber.*, 1924, **57**, [*B*], 356; cf. Einbeck and Jablonski, A., 1923, i, 1099).—Resorcinol has been obtained previously by the author from quebracho tannin (A., 1906, i, 761).

H. W.

Substitution Derivatives of Aurin. C. H. SPIERS (*J. Chem. Soc.*, 1924, **125**, 450—459).—Aurin is most readily isolated from corallin by saturating a solution of the latter in 60% alcohol with sulphur dioxide, and heating the precipitated compound of aurin and sulphurous acid at 130°. The aurin remaining may then be purified by fractional crystallisation from 60% alcohol. *Hexachloroaurin* is obtained as a red powder by boiling with water the product (probably hexachloroaurin sulphate) produced by the action of excess of sulphuryl chloride on aurin in glacial acetic acid solution in presence of ferric chloride. It is insoluble in the usual solvents, but crystallises from anisole in red crystals with a slight golden lustre. *Hexabromoaurin* is obtained similarly from its hydrobromide, which results from the action of excess of bromine on aurin in glacial acetic acid. It dissolves in *o*-chlorophenol, and the solution deposits the *compound* $C_{19}H_8O_3Br_6,C_6H_4Cl{\cdot}OH$ in red crystals with a brassy surface lustre. This loses *o*-chlorophenol at 120° in a vacuum, leaving pure hexabromoaurin as small, red crystals. *Hexabromodiacetylaurin*, obtained by the action of hot acetic anhydride on hexabromoaurin, and also in the cold when a trace of pyridine is present, forms yellow crystals, m. p. 280—290° (decomp.). *Hexabromotriacetylaurin*, colourless crystals of indefinite m. p.

(160—190°), is produced by the action of warm acetic anhydride on the diacetyl derivative in presence of pyridine. *Dibromoaurin* was obtained by the regulated action of bromine on a cold suspension of aurin in glacial acetic acid. It forms deep red, thin, interlocking prisms of a monohydrate, which loses water in a vacuum, leaving small, crimson crystals of the dibromoaurin. By the action of excess of iodine on a solution of aurin in sodium hydroxide, *tetraiododihydroxybenzophenone* (colourless crystals, m. p. 247°, decomp.) was the chief product, together with a little tri-iodophenol, and no iodoaurins could be isolated. *Tetraiododiacetyldihydroxybenzophenone* forms colourless crystals, m. p. 220—222°. *Trimethylaurin* was obtained by diazotising triaminotritolylmethane, and boiling the diazo compound with dilute sulphuric acid. It crystallises from a mixture of ethylene chlorohydrin and water in red crystals with a blue surface colour. *Tribromotrimethylaurin* is obtained by the action of bromine on a solution of trimethylaurin in boiling glacial acetic acid. It crystallises from ethylene chlorohydrin in reddish-brown needles with a slight golden lustre which contain 1 mol. of solvent. The latter is given up at 120° in a vacuum, leaving the tribromotrimethylaurin as small, red crystals. F. G. W.

Interaction of some Aromatic Hydrocarbons, Alcohols, and Aldehydes with Nitrogen Peroxide. L. W. BASS and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1924, **46**, 456—461).—Aromatic hydrocarbons show little tendency to interact with nitrogen peroxide at the ordinary temperature. Exposure to sunlight has very little effect. After heating or long exposure, there is slight evidence of nitration and oxidation. *o*-Nitrobenzaldehyde gave, besides *o*-nitrobenzoic acid, a compound which appears to be *o*-diazobenzoic acid nitrate. Benzyl alcohol was oxidised to a mixture of benzaldehyde and benzoic acid in about equal proportions. Aromatic aldehydes oxidised to acids. With *o*-, *m*-, and *p*-nitrotoluenes there was slight oxidation to *o*-, *m*-, and *p*-nitrobenzoic acids. Anthracene was partly oxidised to anthraquinone. A. B. S.

Chemical Nature of the Naphthenic Acids. I. N. ZELINSKY (*Ber.*, 1924, **57**, [*B*], 42—51).—An attempt has been made to settle the vexed question of the nature of the polycyclic ring present in the naphthenic acids. The latter were converted by a series of mild reactions into hydrocarbons containing the same number of carbon atoms. These were subjected to catalytic dehydrogenation (Zelinsky, A., 1911, i, 958; 1912, i, 167) under conditions such that hexamethylene derivatives were converted into hydrogen and aromatic hydrocarbons whereas the *cyclo*butane, *cyclo*pentane, and *cyclo*heptane rings remained unaffected. It was found that the great majority of the naphthenic acids are not derivatives of *cyclo*hexane.

[With A. TSCHUKSANOWA.]—The initial material was a series of fractions of naphthenic acids obtained from Baku petroleum. The acids were converted into their methyl esters, whereby it was found possible to isolate two fractions the analytical composition of which accorded with that required for methyl heptanaphthenecarboxylate and methyl octanaphthenecarboxylate, respectively, but the wide range of boiling point showed them to be mixtures of isomerides. They were reduced by sodium and alcohol to the corresponding primary alcohols, octanaphthene- and nonanaphthene-alcohols, which were converted by iodine and red phosphorus into the corresponding iodides and subsequently reduced by zinc dust in the presence of aqueous alcohols to the hydrocarbons. The latter were saturated, indifferent towards permanganate and concentrated sulphuric acid, and generally similar to *cyclo*hexane and *cyclo*pentane compounds. When passed over platinum black at 300°, they yielded very little hydrogen.

The preparation of *hexahydro*-o-*xylene* [1 : 2-*dimethyl*cyclo*hexane*], b. p. 127·5—128°, d_{20} 0·7903, d_4^{20} 0·7893, n^{20} 1·4321, is described incidentally; the physical constants of the compound differ widely from those of octanaphthene. H. W.

Chemical Nature of the Naphthenic Acids. II. N. Zelinsky and E. Pokrowskaja (*Ber.*, 1924, **57**, [*B*], 51—58).—An investigation of the octa-, nona-, and deca-naphthenecarboxylic acids along the lines indicated in the preceding abstract. The behaviour of nona-, deca-, and undeca-naphthenes towards palladium black at 300—310° shows that they cannot contain more than small amounts of derivatives of *cyclo*hexane. H. W.

Naphthenic Acids. IV. Metallic Salts of Naphthenic Acids. Y. Tanaka, K. Horiuchi, and G. Ôyama (*J. Chem. Ind. Japan*, 1923, **26**, 1190—1203).—Pure mixed naphthenic acids derived from the waste lyes from the refining of Kurokawa petroleum were separated by distillation into three fractions consisting chiefly of trideca-, tetradeca-, and pentadeca-naphthenic acids, respectively. Metallic salts of these fractions have been prepared, and their solubilities and some other properties have been studied. The solubility increases with decreasing molecular weight of the acid. The lead salts are transparent, resinous solids, m. p. 110—118°. Manganese tridecanaphthenate is a pink powder, soluble in ether, slightly soluble in absolute alcohol (about 2% at 15°), and practically insoluble in cold or hot water. This result contradicts that of von Kożicke and von Pilat (A., 1916, i, 814). Manganese tetradecanaphthenate melts at 61—63°. The lead and manganese salts have a drying action on linseed oil. Chromium salts were obtained in two different modifications, one being a violet powder and the other a green, viscous mass; the former is changed into the latter by heating. Aluminium naphthenate forms a transparent, colourless, and porous mass which can be powdered; it has a waterproofing action. The calcium salts are white, lustrous solids and the magnesium and zinc salts white powders. K. K.

Solid Constituents of Low-temperature Coal Tar. J. Marcusson and M. Picard (*Brennstoff-Chem.*, 1924, **5**, 68—69).—The solid carboxylic acids, isolated from low-temperature coal tar, may be divided into three classes, according as they are soluble in ether, insoluble in ether but soluble in acetone, or insoluble in ether or acetone. They are all aromatic in character and may be sulphonated and nitrated. The content of solid phenols in a tar varies with the method of distillation employed. Naphthalene or anthracene is not present in the primary tar, which contains up to 2% of solid paraffins, a considerable proportion of which is unsaturated. The acetyl value of the neutral portion of the tar both before and after hydrogenation was low, indicating that only small quantities of aldehydes and ketones were present. [Cf. *B.*, 1924, 287.] T. S. W.

Action of Esters on Magnesium Alkyl Halides. G. STADNIKOFF (*Ber.*, 1924, **57**, [*B*], 1—8).—An investigation of the abnormal course of the action of Grignard's reagents on esters whereby esters, ethers, and hydrocarbons are produced in addition to alcohols.

The formation of esters is attributed to the action of the iodomagnesium compounds of the alcohols, formed primarily, on the unchanged ester, thus: $2RMgI+R'\cdot CO_2Et \rightarrow R_2R'CO\cdot MgI+EtO\cdot MgI$ and $R_2R'CO\cdot MgI+R'\cdot CO_2Et \rightarrow R'\cdot CO_2\cdot CR_2R'+EtO\cdot MgI$. Under somewhat unusual conditions, a preparative method of obtaining the esters of complex alcohols is thereby afforded; the examples cited are benzhydryl acetate, b. p. 169—170°/11 mm., m. p. 40—42°, 3-methyl*cyclo*hexyl acetate, b. p. 187—188°/784 mm., menthyl formate, b. p. 110°/20 mm., menthyl acetate, b. p. 131°/40 mm., $[\alpha]_D$ —79·2°, menthyl benzoate, b. p. 189—190°/16 mm., m. p. 54·5—55°, *menthyl iminodiacetate*, $C_{24}H_{43}O_4N$, b. p. 263°/15 mm., m. p. 48—50°, and *menthyl cyanotriacetate*, $C_{36}H_{63}O_6N$, m. p. 80—81°. The iodomagnesium derivatives of the phenols do not react with esters.

The production of simple and mixed ethers is ascribed to the interaction of halogenomagnesium alkoxides on iodides or bromides in accordance with the scheme: $R\cdot O\cdot MgI+CHR'_2I \rightarrow MgI_2+R\cdot O\cdot CHR'_2$, whilst the iodides are themselves formed by the action of magnesium iodide on esters of alcohols of high molecular weight as exemplified by the scheme: $R\cdot CO_2CHPh_2+MgI_2=R\cdot CO_2\cdot MgI+CHPh_2I$. The small proportion of magnesium iodide normally present in a Grignard solution is sufficient to account for the change, since the material which enters into reaction is regenerated. If this explanation be accepted, it is to be expected that hydrocarbons would be formed when an excess of magnesium is employed as indicated by the scheme: $2CHPh_2I+Mg \rightarrow CHPh_2\cdot CHPh_2+MgI_2$. The following experimental evidence in favour of this interpretation is cited. Magnesium ethyl iodide when treated successively with benzhydrol and ethyl acetate in ethereal solution yields benzhydryl ethyl ether, b. p. 157—157·5°/14 mm., and dibenzhydryl ether, m. p. 108—109°. The same products with the addition of tetraphenylethane, m. p. 208—209°, are formed when ethyl acetate is replaced by ethyl formate; the yield of the hydrocarbon is increased by the use of an excess of magnesium. The iodomagnesium compound of triphenylcarbinol is converted to a small extent by ethyl acetate into triphenylmethyl ethyl ether, m. p. 84—85°; the intermediate production of triphenylmethyl iodide is placed beyond doubt by the isolation of triphenylmethyl peroxide from the products of the reaction.

When, in contrast to the usual conditions, the reaction between magnesium phenyl bromide and methyl benzoate is conducted vigorously, considerable amounts of triphenylmethyl methyl ether, m. p. 83—84°, are produced in addition to triphenylcarbinol. The formation of ethers can be considerably restricted, however, by a suitable choice of radicals. Thus magnesium phenyl bromide and benzyl benzoate give only a very small proportion of *triphenylmethyl benzyl ether*, m. p. 106—107°, in boiling ethereal solution, although the yield may be increased by working under increased pressure. Magnesium phenyl bromide and ethyl benzoate give triphenylcarbinol and triphenylmethyl ethyl ether in yields of 42% and 31%, respectively, whereas ethyl formate and magnesium phenyl bromide produce dibenzhydryl ether, benzhydryl ethyl ether, and tetraphenylethane.

Ethyl formate and magnesium α-naphthyl bromide give *di-α-naphthylmethyl ethyl ether*, $C_{23}H_{20}O$, m. p. 134—135°. H. W.

Condensation of Ethyl Oxalate with Nitrotoluenes. I. o-Nitrotoluene. W. WISLICENUS and E. THOMA (*Annalen*, 1924, **436**, 42—68).—By condensing *o*-nitrotoluene with ethyl oxalate in presence of potassium ethoxide, the authors have obtained *o*-nitrophenylpyruvic acid in a better yield (80 as against 55% of the theoretical) than resulted from Reissert's experiments (A., 1897, i, 417; 1898, i, 315). The product was first isolated as a *potassium* derivative, probably of the *aci*nitro form, $NO_2K{:}C_6H_4{:}CH{\cdot}CO{\cdot}CO_2Et$, a dark red substance. In aqueous solution, the colour gradually disappears and potassium *o*-nitrophenylpyruvate is formed. The two desmotropic forms of *o*-nitrophenylpyruvic acid were isolated. The *keto* form,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et,$$

was obtained by decomposing the above red potassium derivative in aqueous solution and formed needles or prisms, m. p. 46—47°. The *enol* form, $NO_2{\cdot}C_6H_4{\cdot}CH{:}C(OH){\cdot}CO_2Et$, m. p. 70—71°, was produced when the decomposition was carried out in ethereal suspension. In alcoholic solution, the two forms exist together as an equilibrium mixture containing 20% of enol, as determined by titration with bromine in the usual way. *Ethyl* β-*bromo*-o-*nitrophenylpyruvate*, obtained by brominating the enol, forms white crystals melting at about 76—82°. It regenerates the parent ester when treated with sodium bisulphite, and with aqueous or alcoholic alkali is partly transformed to a *compound*, $C_{16}H_{13}O_6N_2Br$, m. p. 121—122°. *Ethyl* o-*nitrophenylpyruvate phenylhydrazone* forms yellow needles, m. p. 103·5°, and the *oxime*, colourless needles, m. p. 121—122°. When the ester was treated with ammonia during 4 days, o-*nitrophenylpyruvamide*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}NH_2$, colourless needles, m. p. 165—166°, was obtained. The ester reacts with aniline and various substituted anilines (but not with β-naphthylamine or methylaniline) to form *anils*. Thus with aniline, $NO_2\cdot C_6H_4\cdot CH_2\cdot C(:NPh)\cdot CO_2Et$, red prisms, m. p. 92°; with *p*-toluidine, dark red crystals, m. p. 90·5—91·5°; with *o*-toluidine, orange-red crystals, m. p. 77—78°; with *m*-toluidine, orange-red crystals, m. p. 138°; with 1 : 3 : 4-xylidine, red crystals, m. p. 106·5—107°; with *p*-bromoaniline, dark red prisms, m. p. 136—137°. These compounds should, however, be formulated as the tautomeric anilino-enols, as when they are brominated addition does not take place but bromine enters the nucleus (cf. Hantzsch, A., 1916, i, 12).

o-Nitrophenylpyruvic acid forms colourless leaflets, m. p. 121°. The *methyl* ester was obtained as yellow needles, sintering at 65° and melting between 83° and 87°. It appears to exist largely as the *enol* form, and the pure *keto* form was not isolated. Methylation of the ethyl ester with methyl sulphate gave exclusively *ethyl* o-*nitro-α-methoxycinnamate*, $NO_2\cdot C_6H_4\cdot CH:C(OMe)\cdot CO_2Et$, scales, m. p. 46—47°. This gave a *dibromide*,

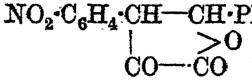
$$NO_2\cdot C_6H_4\cdot CHBr\cdot CBr(OMe)\cdot CO_2Et,$$

m. p. about 98°, which by boiling with alcohol was converted into *ethyl β-bromo*-o-*nitro-α-methoxycinnamate*, colourless prisms, m. p. 79—80°. o-*Nitro-α-methoxycinnamic acid* itself has m. p. 160—161°; its *methyl* ester, 67·5—68°. *α-Ethoxy*-o-*nitrophenylcinnamic acid* and its *methyl* ester were obtained in a similar way, using ethyl iodide as ethylating agent, and melted at 146—147° and 49—50°, respectively. When ethyl *o*-nitrophenylpyruvate was methylated with methyl iodide, the *C*-methyl derivative, namely *ethyl* o-*nitrophenyl-β-methylpyruvate*, was produced. This compound is an oil and was isolated as its *phenylhydrazone*,

$$NO_2\cdot C_6H_4\cdot CHMe\cdot C(:N\cdot NHPh)\cdot CO_2Et,$$

white needles, m. p. 131·5—132·5°; a by-product, presumably the phenylhydrazone of the dimethyl derivative, forms yellow scales, m. p. 136°.

Ethyl *o*-nitrophenylpyruvate was benzoylated to give the O-*benzoyl* derivative, $NO_2\cdot C_6H_4\cdot CH:C(OBz)\cdot CO_2Et$, small tablets, m. p. 46—47°. The corresponding *acetyl* derivative forms prisms, m. p. 95—96°. When the ester is treated with benzaldehyde the *lactone*,



$$\begin{array}{l} NO_2\cdot C_6H_4\cdot CH\text{—}CH\cdot Ph \\ \quad\quad\quad\quad | \quad\quad\quad > O \\ \quad\quad\quad\quad CO\text{—}CO \end{array}$$

, is formed, m. p. 174—176°, whilst with sodium nitrite, contrary to what Reissert has stated (*loc. cit.*), it yields *ethyl* o-*nitrophenyl*-β-iso*nitrosopyruvate*,

$$NO_2\cdot C_6H_4\cdot C(:NOH)\cdot CO\cdot CO_2Et,$$

colourless, tetrahedral crystals, m. p. 120·5—121·5° (decomp.). It combines with diazobenzene to form a yellow *compound*. Attempts to prepare ethyl *o*-nitrophenyl-β-methylpyruvate by interaction of ethyl oxalate and *o*-nitroethylbenzene failed.

II. Condensation of Ethyl Oxalate and p-Nitrotoluene. [With F. Schultz.]—This reaction was carried out in the same way as that just described, but when ethyl oxalate was used there were always formed some *pp'*-dinitrostilbene and dinitrodibenzyl as by-products (cf. Reissert, *loc. cit.*). These were not produced when methyl oxalate was used, nor from *p*-nitrotoluene and potassium or sodium ethoxide alone under the same conditions. *Ethyl* p-*nitrophenylpyruvate* forms a red *potassium* derivative resembling the *o*-isomeride described above. The free ester appears to exist solely in the enolic form as an intensely yellow substance, crystallising in rectangular prisms, m. p. 106°. The *acid* has m. p. 194° and gives a *pyridine* salt, yellowish-green needles, m. p. 150°. When the ethyl ester is reduced with tin and hydrochloric acid, it gives *p*-aminophenyl-lactic acid, m. p. 188° (Erlenmeyer, A., 1883, 994). *Ethyl* p-*nitrophenylpyruvate phenylhydrazone* forms yellowish-green prisms, m. p. 113°, and when heated with alcoholic sulphuric acid suffers intramolecular condensation, forming *ethyl* 3-p-*nitrophenylindole-2-carboxylate*, yellow, rectangular leaflets, m. p. 216°. The *anil* of ethyl *p*-nitrophenylpyruvate forms orange-red scales, m. p. 76°; the corresponding derivative with *o*-toluidine, orange-yellow needles, m. p. 85°; with *p*-toluidine, scarlet-red prisms, m. p. 97°; with α-naphthylamine, orange-red leaflets, m. p. 113°; with β-naphthylamine, scarlet-red, rectangular scales, m. p. 137°; with anthranilic acid, yellow needles, m. p. 194°. When the ester is treated with *o*-diamines quinoxalines are formed; thus with 1 : 3 : 4-tolylenediamine 2-*hydroxy*-3-p-*nitrobenzyl*-7-*methylquinoxaline* was obtained, m. p. 270°. With *o*-aminophenol 2-*keto*-3-p-*nitrobenzylbenzoxazine*, a deep red substance, m. p. 192°, was produced. By interaction of *p*-nitrotoluene and methyl oxalate, *methyl* p-*nitrophenylpyruvate* was prepared. This compound resembles the ethyl ester and crystallises in yellow pyramids, m. p. 149°. The β-*bromo* derivative has m. p. 114—115°, the *oxime*, 172—173°, and the *phenylhydrazone* about 136—145°.

III. Condensation of Ethyl Oxalate and 1-Nitro-2-methylnaphthalene. [With E. MUNDINGER.]—The sole product of this reaction under normal conditions was *ethyl* 1-*nitro*-2-*naphthylpyruvate*, but if double the usual quantity of potassium ethoxide were used 1 : 1′-*dinitro*-2 : 2′-*dinaphthylethane*, yellow prisms, m. p. 251°, was chiefly formed (cf. Mayer and Oppenheimer, A., 1916, i, 816). *Ethyl* 1-*nitro*-2-*naphthylpyruvate* was isolated in the two desmotropic forms. The *ketonic* form was obtained by decomposing its bisulphite compound and formed colourless needles, m. p. 84°. The *enol* was prepared by treating the potassium compound in ethereal suspension with mineral acid and separated as yellow crystals, m. p. 135°. In alcoholic solution, the two forms exist as an equilibrium mixture containing about 58% of enol. The ketonic form yields an additive *compound* with methyl alcohol, m. p. 76°. The ester forms a *copper* compound when treated with copper acetate, a brown precipitate, m. p. 182°. Its O-*benzoyl* derivative crystallised in yellow prisms, m. p. 107°; its O-*methyl* derivative in pearly prisms, m. p. 114—115°; the corresponding methoxy *acid* melts at 178°. The *anil* of ethyl nitronaphthylpyruvate forms yellow prisms, m. p. 116—117°. When the ester is treated with *o*-aminophenol an *oxazine* corresponding with the one described under II is formed (yellow prisms, m. p. 179°), and when it is reduced with zinc amalgam *ethyl* α-*naphthindolecarboxylate*

(m. p. 173—174°, free *acid*, m. p. 213°) is obtained (cf. Mayer and Oppenheimer, A., 1919, i, 17). W. A. S.

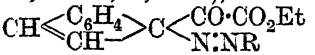
Studies in the Indene Series. I. Derivatives of Indeneglyoxylic Ester and of Indene-1-carboxylic Acid [Indene-3-carboxylic Acid]. W. Wislicenus and W. Hentrich (*Annalen*, 1924, **436**, 9—41).—Ethyl indene-1-glyoxylate,

$$\mathrm{CH}{<}\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CH}{-}{-}\end{matrix}{>}\mathrm{CH{\cdot}CO{\cdot}CO_2Et},$$

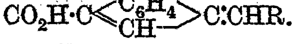
is methylated less readily than the corresponding fluorene derivative (see p. 398) and gives a product which cannot be isolated in a pure condition and was therefore directly hydrolysed; 55% of the calculated yield of 3-methylindene (b. p. 198·5°, d_4^{20} 0·9640) was thus obtained together with tarry by-products, transference of the double bond having occurred (cf. Courtot, A., 1915, i, 392). In the same way, 3-ethylindene was prepared; yield 43% of the theoretical, b. p. 215—216° (cf. von Braun, A., 1918, i, 111). The intermediate ethyl indeneglyoxylate could not be obtained in a pure state. 1-*Benzylidene*-3-*ethylindene* crystallises in yellow, rectangular scales, m. p. 57—58°. The *benzylidene* derivative of 3-benzylindene has m. p. 137·5°; the corresponding derivative from *p*-tolualdehyde forms bundles of yellow needles, m. p. 94°, and from cinnamaldehyde orange prisms, m. p. 161—162°. *Ethyl* 3-*benzylindene*-1-*glyoxylate* forms orange, rectangular tablets, m. p. 130°. This compound, unlike its congeners, is stable. 3-*Allylindene*, b. p. 138°/27 mm., prepared by the same general method, is very easily oxidised by the air. Attempts to prepare *s*-di-indenylethane failed.

Ethyl indeneglyoxylate behaves in a similar way to the corresponding fluorene compound when treated with primary amines (cf. p. 398). The *anil*, $C_9H_7C(:NPh){\cdot}CO_2Et$, forms brownish-red prisms, m. p. 142°; the *o*-toluidine derivative (unstable), dark brown prisms, m. p. 107—108°; the α-naphthylamine derivative, reddish-brown crystals, m. p. 127°. The *phenylhydrazone* forms dull yellow cubes, m. p. 69°; it decomposes when kept. The *oxime* forms a yellow, crystalline powder, m. p. 204° (decomp.).

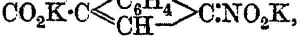
When ethyl indeneglyoxylate reacts with one molecular proportion of hydrazine hydrate, an additive *compound* is formed to which the authors ascribe the formula $C_9H_7{\cdot}C(OH)(NH{\cdot}NH_2){\cdot}CO_2Et$. This is quite stable, m. p. 184°, and decomposes when heated above its melting point. When two molecular proportions of hydrazine hydrate were used the product was the *hydrazide* of the above, m. p. 218° (decomp.). Bromination of the ester gave a definite product only when four atomic proportions of bromine were taken up, 1 : 2 : 3-*tribromohydrindene*-3-*glyoxylic acid*, white rosettes, m. p. 101°, being formed. For this reason, attempts to determine the proportion of enol in ethyl indeneglyoxylate by Meyer's bromine titration method failed.

Ethyl indeneglyoxylate reacts with diazonium compounds, giving, not a hydrazone of the hitherto unknown indenone like the corresponding fluorene derivative (Wislicenus and Densch, A., 1902, i, 291), but a compound for which the structure  $CH{<}\substack{C_6H_4\\CH-}{>}C{<}\substack{CO\cdot CO_2Et\\N:NR}$ is proposed.

Ethyl 3-methylindene-1-glyoxylate gives a similar compound. This formula explains the fact that the compound dissolves readily in aqueous alkali with loss of the carbethoxy group. *Ethyl* 1-*benzeneazoindene*-1-*glyoxylate* forms dark red crystals, m. p. 146°. Similar products were obtained by interaction with *p*-nitrobenzenediazonium chloride (scarlet-red needles, m. p. 209°, decomp.), and with *m*-nitrobenzenediazonium chloride (red, amorphous powder, m. p. 201—202°, decomp.). From the latter an *acid* was obtained by dissolving it in cold dilute aqueous potassium hydroxide and reprecipitating, m. p. 151—153° (decomp.).

Indene-3-*carboxylic acid* was prepared by oxidising sodium indene-1-glyoxylate (Thiele, A., 1901, i, 76) with hydrogen peroxide (yield variable, 30—65%). The product melted at 160° and was found to be identical with that obtained by Weissgerber (A., 1911, i, 623). Transposition of the double bond has again taken place. The *hydrazide*, $C_9H_7\cdot CO\cdot NH\cdot NH_2$, forms rectangular, colourless leaflets, m. p. 186°; its *hydrochloride*, needles, darkens at 245° and decomposes at 263°. The hydrazide reacts readily with aromatic aldehydes, but not so smoothly with ketones, to give well crystallised *hydrazones*; thus with benzaldehyde, it forms white needles, m. p. 272—273°; with *o*-nitrobenzaldehyde, pale yellow needles, m. p. 215° (decomp.); with *p*-tolualdehyde, long, colourless needles, m. p. 254—255° (decomp.); with salicylaldehyde, flexible, yellow needles, m. p. 267° (decomp.); with cinnamaldehyde, sulphur-yellow leaflets, m. p. 239—242° (decomp.); with furfuraldehyde, yellow, rectangular, prismatic needles, m. p. 234°; with oxindole-3-aldehyde, yellow, clustered needles, darkening at 280°, m. p. 293° (decomp.). The *diacetyl* derivative of the hydrazide forms colourless needles, m. p. 147°; the *benzoyl* derivative, leaflets, m. p. 212—213°; a by-product, presumably the *dibenzoyl* derivative, has m. p. 253—255°. The β-*phenylhydrazide* of indene-3-carboxylic acid, $C_9H_7\cdot CO\cdot NH\cdot NHPh$, forms yellow needles, m. p. 188°. The *amide*, $C_9H_7\cdot CO\cdot NH_2$, forms yellow leaflets, m. p. 180°. The *anilide* crystallises in yellow prisms, m. p. 158°. Indene-3-carboxylic acid readily reacts with aldehydes in methyl-alcoholic potassium hydroxide solution to form highly coloured fulvene derivatives of the general formula,  $CO_2H\cdot C{<}\substack{C_6H_4\\CH-}{>}C:CHR$. 1-*Benzylideneindene*-3-*carboxylic acid* forms yellow needles, m. p. 222°; the 3-*furfurylidene* derivative, brownish-red, prismatic needles, m. p. 250°; the 3-*cinnamylidene* derivative is an orange powder, m. p. 235°. *Ethyl* 3-*carboxyindene*-1-*glyoxylate* forms orange-red prisms, m. p. 138·5° (decomp.). The *acid* forms a red precipitate, m. p. 199°. Its *ethyl* ester, obtained by interaction of ethyl indenecarboxylate with ethyl oxalate, crystallises in rectangular prisms, m. p. 116°. By treating the potassium derivative of potassium indene-3-carboxylate with ethyl bromide it was hoped to obtain 1-ethylindene-3-carboxylic acid, but actually the product was mainly 3-ethylindene. The potassium compound of ethyl indenecarboxylate reacts with two molecular proportions of benzenediazonium chloride, giving an orange-red *substance*, m. p. 163°. A similar compound with *p*-nitrodiazobenzene forms a red powder, m. p. 223—225° (decomp.).

Ethyl 3-methylindene-2-carboxylate (Thiele and Rüdiger, A., 1906, i, 586) reacts with ethyl oxalate in presence of potassium ethoxide to give *ethyl 3-methyl-2-carbethoxyindene-1-glyoxylate*, $CO_2Et{\cdot}C_9H_5Me{\cdot}CO{\cdot}CO_2Et$, the potassium compound of which forms pearly leaflets darkening at 200° and melting with decomposition at 215°. The free ester crystallises in pale yellow needles, m. p. 123—125° (only if rapidly heated). The corresponding compound from the methyl methylindenecarboxylate forms yellow needles, m. p. 134—135°.

II. Indene-3-carboxylic Acid. [With G. MANTHE.]—Methyl indene-3-carboxylate (Weissgerber, A., 1911, i, 623) on methylation readily gave (yield 66%) *methyl 1-methylindene-3-carboxylate*, a yellow oil, b. p. 127°/14 mm., which forms an unstable *dibromide*, m. p. 87—88°, b. p. 170—185°/11 mm. When the ester was hydrolysed 3-methylindene was obtained. In the same way, *ethyl 1-methylindene-3-carboxylate* was prepared (yield 80%, b. p. 132—136°/16 mm.) and likewise hydrolysed. *Ethyl 1-ethylindene-3-carboxylate* (yield 70%, b. p. 148—150°/19 mm.) gave similarly ethylindene in 70% yield. *Ethyl 1-benzylindene-3-carboxylate* (yellow, viscous oil, b. p. 240°/20 mm.) gave a good yield (80%) of benzylindene. Attempts to prepare by this method both *s*-di-indenylethane and 1 : 1′-di-indenyl failed. When the potassium compound of ethyl indenecarboxylate was treated with one molecular proportion of benzoyl chloride, a blue compound still containing potassium was produced, whilst when an excess of benzoyl chloride was used a *dibenzoyl* derivative was formed (yellow prisms, m. p. 166°). A similar derivative was produced when *m*-nitrobenzoyl chloride was used (yellow needles, m. p. 164°). The *dibenzoyl* derivative of the methyl ester forms a yellow powder, m. p. 182°. Indene-3-carboxylic acid, but not its ethyl ester, reacts with ethyl nitrate in presence of potassium ethoxide to give *di-potassium 1-nitroindene-3-carboxylate*,  $CO_2K{\cdot}C\Big<{}^{C_6H_4}_{CH\!-\!-}\Big>C{:}NO_2K$, of which the *lead* salt was also prepared.

III. 1-Nitroindene. [With K. PFEILSTICKER.]—Indene was treated with ethyl nitrate and potassium ethoxide and the hitherto unknown *1-nitroindene* obtained as a *potassium* derivative, $CH\Big<{}^{C_6H_4}_{CH\!-\!-}\Big>C{:}NO_2K$, an unstable, yellow, crystalline substance. The free nitroindene was obtained as a crystalline, greenish-yellow precipitate, m. p. 50°, which was too easily decomposed to be recrystallised. This is the *aci*-form. It decomposes without changing over into the true nitro compound. It forms more stable condensation products with aromatic aldehydes, but not with ketones, in presence of sulphuric acid. *3-Nitro-1-benzylideneindene* forms orange leaflets, m. p. 139°; *3-nitro-1-tolylideneindene*, red crystals, m. p. 105°; similar derivatives with p-*nitrobenzaldehyde* (red needles, m. p. 218—220°) and *cinnamaldehyde* (deep red crystals, decomposing at 208°) were prepared. Potassium nitroindene was converted by treatment with benzoyl chloride into 1-*nitro*-3-*benzoylindene*, yellow rhombs, m. p. 121°. The above benzylidene derivatives were reduced with tin and hydrochloric acid, giving the corresponding benzylaminoindenes. Nitroindene itself gave an unstable product. 1 : 3- (or 3 : 1-)*Benzylaminoindene* is a rapidly oxidising oil; its *hydrochloride*, microscopic crystals, m. p. 237°; its *acetyl* derivative, needles, decomposing at 243°. *Cinnamylaminoindene hydrochloride* melts at 242—245°, and its *acetyl* derivative decomposes at 267°. W. A. S.

Condensations in the Arylacetonitrile Series. I. Formyl-α-naphthylacetonitrile, Ethyl Formyl-α-naphthylacetate, and Ethyl α-Naphthyloxalacetate. W. Wislicenus, G. Butterfass, and G. Koken (*Annalen*, 1924, **436**, 69—100).—*Formyl-α-naphthylacetonitrile* was obtained by interaction of naphthylacetonitrile (Mayer and Oppenheimer, A., 1916, i, 816) and ethyl formate. The *potassium* compound forms a yellow powder. The free nitrile is an imperfectly crystalline, colourless mass, m. p. 130°, giving a brown *copper* salt. Titration with bromine indicated that from 95·8 to 99·7% (in different preparations) existed in the enolic form. It should therefore be formulated as hydroxymethylenenaphthylacetonitrile, $C_{10}H_7\cdot C(CN){:}CH\cdot OH$ (cf. Wislicenus, A., 1896, i, 522). It forms an *anilide*, white leaflets, m. p. 152—154°; p-*toluidide*, prisms, m. p. 142°; *semicarbazide*, diamond-shaped scales, m. p. 172—173°; and *hydroxylamide*, needles, m. p. 111°. It reacts with phenyl*iso*cyanate only at a much higher temperature than similar compounds (cf. Wislicenus, *loc. cit.*) to form the *carbanilate*, $NHPh\cdot CO\cdot O\cdot CH{:}C(C_{10}H_7)\cdot CN$, pale yellow needles, m. p. 158—159° (decomp.).

Various derivatives of ethyl formyl-α-naphthylacetate (Wislicenus and Elvert, A., 1917, i, 202) which could not be obtained directly by simultaneous hydrolysis and esterification of the nitrile, were prepared. The *anilide* forms quadratic prisms, m. p. 94—96°; the p-*toluidide*, glistening crystals, m. p. 90—91°. The latter derivative when heated at 250—260° suffered intramolecular condensation and 3-α-*naphthyl*-4-*hydroxy*-6-*methylquinoline* was formed (needles, m. p. 302—305°, subliming at a somewhat higher temperature; *picrate*, m. p. 140—145°). When ethyl formylnaphthylacetate was reduced by Clemmensen's method, it gave a mixture of α-(α-*naphthyl*)*hydracrylic acid* (crystalline powder, m. p. 112°) and *ethyl α-naphthylacrylate* (an oil, b. p. 220—230°/12 mm.). α-*Naphthylacrylic acid* forms needles, m. p. 152—154°. Ethyl formyl-α-naphthylacetate was alkylated and found to give invariably *O*-derivatives. The *methyl* derivative formed an indefinitely crystalline mass, m. p. 63—64°, and the *ethyl* derivative needles, m. p. 75°.

Ethyl α-naphthylacetate and ethyl oxalate were condensed together in the usual way to produce *ethyl α-naphthyloxalacetate*,

$C_{10}H_7\cdot CH(CO_2Et)\cdot CO\cdot CO_2Et$, a yellow oil which decomposes when distilled. Its *potassium* salt forms silky leaflets which decompose at 220—223°; its *copper* salt has a m. p. dependent on the solvent from which it is recrystallised. With phenylhydrazine, *ethyl* 1-*phenyl*-4-α-*naphthyl*-5-*pyrazolone*-3-*carboxylate* is obtained as microscopic leaflets, m. p. 213—214°. When the ester is heated at 180—186° it loses carbon monoxide, forming *ethyl α-naphthylmalonate* (clustered prisms, m. p. 59—60°), the sodium derivative of which, by interaction with ethyl bromoacetate and subsequent hydrolysis, gives *α-naphthylsuccinic acid*, rectangular scales, m. p. 206° (decomp.).

II. Formyl-β-naphthylacetonitrile and Ethyl Formyl-β-naphthylacetate. [With H. Riethmüller.]—The β-naphthyl derivative resembles the α-isomeride described above. It crystallises in leaflets, m. p. 181—182°, gives a brown *copper* salt, and appears to exist mainly in the *enolic* form. Its O-*benzoyl* derivative forms needles, m. p. 188°; the *anilide*, yellow needles, m. p. 185°; p-*toluidide*, yellowish-green leaflets and needles, m. p. 199—201°; *oxime*, leaflets, m. p. 135—136°; compound with *phenylcarbimide*, needles, m. p. 178° (decomp.). It reacts with benzenediazonium chloride to form β-*naphthylglyoxylonitrile phenylhydrazone* (yellow needles, m. p. 195—196°), the formyl group being displaced. When formyl-β-naphthylacetonitrile is treated with bromine, an impure *bromo* derivative, m. p. 162—164°, is obtained, whilst with iodine its potassium compound in methyl-alcoholic solution gives s-*di*-β-*naphthylsuccinonitrile*, $C_{10}H_7\cdot CH(CN)\cdot CH(CN)\cdot C_{10}H_7$, colourless prisms, m. p. 246—249°. The free nitrile in aqueous methyl alcohol with iodine and sodium hydroxide gives s-*di*-β-*naphthyldicyanoethylene*, $C_{10}H_7\cdot C(CN){:}C(CN)\cdot C_{10}H_7$, yellow needles, m. p. 204°. The latter compound was also obtained by treating β-naphthylacetonitrile in a similar way.

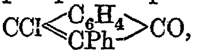
Ethyl formyl-β-naphthylacetate gave on reduction and hydrolysis the corresponding α-(β-*naphthyl*)-β-*hydroxypropionic acid*, $OH\cdot CH_2\cdot CH(C_{10}H_7)\cdot CO_2H$, which formed clustered crystals, m. p. 154—156°. Ethyl formyl-β-naphthylacetate gives an *anilide*, yellow needles, m. p. 91—92°; with phenylhydrazine it forms, not the expected phenylhydrazone, but 1-*phenyl*-4-β-*naphthyl*-5-*pyrazolone*, colourless needles, m. p. 219—220°, yet with 2 : 4-*dinitrophenylhydrazine* the second reaction does not take place and the corresponding *dinitrophenylhydrazone* only is formed, orange-yellow crystals, sintering at 110° and melting between 115° and 118°.

III. Ester Condensations with Benzyl Cyanide. [With H. Eichert and M. Marquardt.]—Cyanodeoxybenzoin,

$$C_6H_5\cdot CO\cdot CH(CN)\cdot C_6H_5,$$

was obtained by interaction of ethyl benzoate, benzyl cyanide, and metallic potassium in yields superior to those of earlier workers (Walther and Schickler, A., 1897, i, 522; Bodroux, A., 1911, i, 545). It forms colourless scales, m. p. 91—92°, and gives an *anil*, yellow needles, m. p. 201°. By simultaneous hydrolysis and esterification *ethyl benzoylphenylacetate* (needles, m. p. 90—91°; b. p. 220—225°/

13 mm.) and the corresponding *methyl* ester (rosettes of colourless prisms, m. p. 74—75°) were obtained. Both compounds exist in solution in the two desmotropic forms; in the case of the *methyl* ester, the enolic form accounts for 4—5% of the whole. Ethyl benzoylphenylacetate heated with aniline forms *benzoylphenylacetanilide*, Bz·CHPh·CO·NHPh, colourless needles, m. p. 168°; with phenylhydrazine it gives either the *phenylhydrazone* (needles, m. p. 173—174°) or, at a higher temperature, 1 : 3 : 4-*triphenyl*-5-*pyrazolone*, leaflets, m. p. 193—194°. When it was treated with phosphorus pentachloride, a mixture of 3-*chloro*-2-*phenylindone*,


$CCl<\begin{matrix}C_6H_4\\ CPh\end{matrix}>CO$

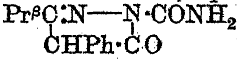
orange-red needles, m. p. 93—94°, b. p. 205—210°/13 mm., and *ethyl chlorobenzoylphenylacetate*, needles, m. p. 44—45°, b. p. 225—230°/12 mm., was formed. The latter compound was also obtained by direct chlorination of the ester.

Ethyl benzoylbenzoate (A., 1908, i, 994) was similarly condensed with benzyl cyanide to form *benzoylbenzoylphenylacetonitrile*, crystallising from alcohol in colourless needles or scales, m. p. 214°, and from benzene in irregular crystals, m. p. 188°. Neither is the enolic form. The compound resists hydrolysis, and forms a loose compound with hydrogen chloride. It is unaffected by hydrazine, aniline, and the like, and the only derivative obtained was *benzoylbenzoylphenylmethylacetonitrile*, $Bz{\cdot}C_6H_4{\cdot}CO{\cdot}CMePh{\cdot}CN$, prisms, m. p. 145°.

Ethyl *iso*butyrate and benzyl cyanide condensed to form *phenyl*iso*butyroacetonitrile* (β-*keto*-α-*phenyl*-γ-*methylvaleronitrile*),

$$CHMe_2{\cdot}CO{\cdot}CHPh{\cdot}CN,$$

a yellow oil, b. p. 154—156°/13 mm. The *bromo* derivative (needles, m. p. 192°), *phenylhydrazone* (needles, m. p. 109°), *hydrazone* (needles, m. p. 102°), *oxime* (needles, m. p. 85°), and *semicarbazone* (needles, m. p. 147°) were prepared. By simultaneous hydrolysis and esterification, *ethyl* α-*phenyl*iso*butyroacetate* (oil, b. p. 150—160°/13 mm.) and the corresponding *methyl* ester (leaflets, m. p. 52°) were obtained. The *acid*, $CHMe_2{\cdot}CO{\cdot}CHPh{\cdot}CO_2H$, forms colourless needles, m. p. 159°. From the ester with phenylhydrazine 1 : 4-*diphenyl*-3-iso*propylpyrazolone* (colourless needles, m. p. 191°) and with hydrazine 4-*phenyl*-3-iso*propylpyrazolone* (m. p. 192°) were obtained, whilst with semicarbazide, 4-*phenyl*-3-iso*propyl*-5-*pyrazolone*-1-*carboxylamide*,


$\begin{matrix}Pr^{\beta}C{:}N & — & N{\cdot}CONH_2\\ | & & |\\ CHPh & \cdot & CO\end{matrix}$

m. p. 187°, solidified again at 188—189°, remelted at 318—320°, was produced. When the ester was hydrolysed with dilute sulphuric acid, benzyl *iso*propyl ketone (b. p. 232—235°; cf. Blaise, A., 1901, i, 252) was obtained.

Ethyl diphenylacetate and benzyl cyanide condense to give *diphenylacetophenylacetonitrile* (β-*keto*-αγγ-*triphenylbutyronitrile*), $CPh_2{\cdot}CO{\cdot}CHPh{\cdot}CN$ (needles, m. p. 97°), which gives a *phenylhydrazone* (needles, m. p. 167°) and a *hydrazone* (needles, m. p. 135°). *Ethyl* β-*keto*-αγγ-*triphenylbutyrate* forms scales, m. p. 109—110°, and gives 4-*phenyl*-3-*diphenylmethyl*-5-*pyrazolone*, m. p. 232—233°, with hydrazine.

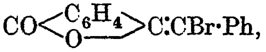
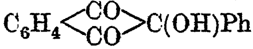
W. A. S.

Fluorene- and 2-Nitrofluorene-9-glyoxylic Esters. W. Wislicenus and H. Weitemeyer (*Annalen*, 1924, **436**, 1—9).—*Fluorene-9-glycollic acid*, which the authors (A., 1921, i, 511) failed to obtain from its ester, prepared by reducing ethyl fluorene-9-glyoxylate with aluminium amalgam, owing to simultaneous dehydration to dibenzofulvene-ω-carboxylic acid, is produced directly when the reduction is carried out by Clemmensen's method. *Methyl fluorene-9-glycollate* forms white needles, m. p. 96°. When ethyl fluorene-9-glyoxylate or the free acid is oxidised with hydrogen peroxide following Reissert's procedure, it gives, not the expected fluorene-9-carboxylic acid, but exclusively fluorenone. The product obtained by Wislicenus and Densch (A., 1902, i, 291) by methylating ethyl fluoreneglyoxylate is the *C*-methyl derivative, as it may be easily hydrolysed to 9-methylfluorene. Ethyl fluoreneglyoxylate may be nitrated: the glyoxylyl group is displaced and 2 : 9-*dinitrofluorene* formed. This substance crystallises in white needles which turn yellow on exposure to light, m. p. 136°. It decomposed when heated above its melting point, giving 2-nitrofluorene. The same compound was obtained, and its constitution proved, by further nitrating both 9-nitrofluorene (Wislicenus and Waldmuller, A., 1908, i, 973) and ethyl 2-nitrofluorene-9-glyoxylate. Although 9-nitrofluorene reacts with alcoholic potassium hydroxide, the 2 : 9-dinitro derivative is insoluble in this reagent and is unable to pass over into an *aci*-form. Ethyl fluorene-9-glyoxylate yields an *anil*, $C_{13}H_9\cdot C(:NPh)\cdot CO_2Et$, orange-yellow crystals, m. p. 137°, and corresponding derivatives with *p*-toluidine and β-naphthylamine (m. p. 156°). With hydrazine, on the other hand, the ethoxy group is displaced and a *hydrazide* formed, $C_{13}H_9\cdot CO\cdot CO\cdot NH\cdot NH_2$, small, yellow crystals, m. p. above 350°. This compound reacts with benzaldehyde to form a *benzylidene* derivative, crystallising in needles which decompose above 350°, and with acetone to give the *hydrazone*, $C_{13}H_9\cdot CO\cdot CO\cdot NH\cdot N:CMe_2$, m. p. 216°.

In 2-nitrofluorene, as in 2 : 7-dibromofluorene (Sieglitz, A., 1920, i, 605), the methylene group is more reactive than in fluorene itself. Thus when a warm solution of 2-nitrofluorene in benzene is added to a mixture of ethyl oxalate and potassium ethoxide, the potassium salt of 2-nitrofluorene-9-glyoxylic ester is immediately thrown down. *Ethyl 2-nitrofluorene-9-glyoxylate* forms yellow crystals, m. p. 143°. It gives coloured precipitates with heavy metals. The ester must be hydrolysed at temperatures below 80°, otherwise scission takes place and 2-nitrofluorene is reproduced. The free acid, $NO_2\cdot C_{13}H_8\cdot CO\cdot CO_2H,H_2O$, forms minute yellow crystals, m. p. 183°. The *methyl* ester has an indefinite melting point, about 120°. The ethyl ester yields a *phenylhydrazone*, yellowish-brown crystals, m. p. 192°; an *anil*, dark red crystals, m. p. 162°, and corresponding derivatives with *p*-toluidine and β-naphthylamine, m. p. 164° and 187°, respectively. Like the unsubstituted fluoreneglyoxylic ester, it gives a *benzoyl* derivative, $NO_2\cdot C_{13}H_7:C(OBz)\cdot CO_2Et$ (cf. Wislicenus and Densch, *loc. cit.*), minute yellow crystals, m. p. 137—138°, easily decomposed again by solution in alcoholic potassium hydroxide. W. A. S.

Equilibrium in the System, Sodium Phthalate–Sodium Sulphate–Water. H. W. FOOTE and S. B. SMITH (*J. Amer. Chem. Soc.*, 1924, **46**, 84—88).—The solubility relations of the system, sodium phthalate–sodium sulphate–water have been determined at 0°, 25°, and 35°. The transition temperature at the quintuple point, where the solid phases are anhydrous sodium sulphate, the decahydrate of sodium sulphate, and hydrated sodium phthalate, has been found to be 23°. When crystallised from water at the ordinary temperature, sodium phthalate has the composition represented by $2Na_2C_8H_4O_4,7H_2O$. J. F. S.

Unsaturated Lactones. S. GABRIEL, L. KORNFELD, and C. GRUNERT (*Ber.*, 1924, **57**, [*B*], 302—306).—An investigation of the behaviour of arylidene- and alkylidenephthalides containing a bromine atom in the side chain towards sodium methoxide.

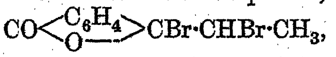
α-*Bromobenzylidenephthalide*,  $CO<^{C_6H_4}_{O}>C{:}CBr\cdot Ph$, quadratic leaflets, m. p. 193°, is obtained by heating the corresponding dibromide in a current of carbon dioxide at 140—150° until hydrogen bromide ceases to be evolved. It is transformed by a solution of sodium in methyl alcohol into *hydroxydiketophenylhydrindene*,  $C_6H_4<^{CO}_{CO}>C(OH)Ph$, yellow needles, m. p. 192° (in a vacuum), which, when dissolved in alkali hydroxide and exposed to the air, passes into *benzil*-o-*carboxylic acid*, $COPh\cdot CO\cdot C_6H_4\cdot CO_2H$, m. p. 140—141°. *Methoxydiketophenylhydrindene* crystallises in needles, m. p. 114°. α-Bromobenzylidenephthalide is not appreciably affected by boiling water, but is transformed by boiling potassium hydroxide solution (20%) into benzhydroldicarboxylic acid, $CO_2H\cdot C_6H_4\cdot CPh(OH)\cdot CO_2H$.

α-Bromo-*p*-tolylidenephthalide is converted in a similar manner into 4′-*methylbenzil-2-carboxylic acid*, small needles, m. p. 143°.

α-*Bromopropiophenone*-o-*carboxylic acid*,

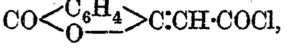
$$CO_2H\cdot C_6H_4\cdot CO\cdot CHBrMe,$$

needles, m. p. 110°, is transformed by potassium hydroxide into *hydroxydiketomethylhydrindene*, which readily becomes oxidised on exposure to air and by a saturated solution of hydrogen bromide in glacial acetic acid to the *dibromo* compound,



$$CO<^{C_6H_4}_{O}>CBr\cdot CHBr\cdot CH_3,$$

rhombic crystals, m. p. 97—99°. αα-*Dibromopropiophenone*-o-*carboxylic acid*, needles, m. p. 140°, when treated successively with boiling water and phenylhydrazine, gives a *phenylhydrazone*, $CO_2H\cdot C_6H_4\cdot CO\cdot C({:}N\cdot NHPh)\cdot Me$, or $CO_2H\cdot C_6H_4\cdot C({:}N\cdot NHPh)\cdot CO\cdot Me$, quadratic plates, m. p. 219° (decomp.).

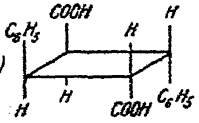
Phthalylideneacetic acid is converted by phosphoryl chloride and phosphorus pentachloride into *phthalylideneacetyl chloride*,  $CO<^{C_6H_4}_{O}>C{:}CH\cdot COCl$, long needles, m. p. 158°, which is transformed by a small quantity of the respective alcohols into the corresponding *methyl* ester, quadratic leaflets, m. p. 168° (decomp.), and *ethyl* ester, m. p. 132—134°; when boiled with an excess of the alcohols, however, it yields *methyl o-carboxybenzoylacetate*, $CO_2Me\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO_2Me$, m. p. 73°, or the corresponding *ethyl* ester. *Methyl diketohydrindenecarboxylate*, $C_6H_4<\substack{CO\\CO}>CH\cdot CO_2Me$, is prepared by the action of potassium hydroxide solution at 0° on the dimethyl ester or of sodium methoxide on methyl phthalylideneacetate. The diethyl ester is converted similarly into ethyl diketohydrindenecarboxylate, m. p. 76°. H. W.

Fluorene Series. VIII. Synthesis of Fluorenone-1-carboxylic Acid. A. SIEGLITZ (*Ber.*, 1924, **57**, [*B*], 316—317).—2′-Aminobenzophenone-2-carboxylic acid is diazotised in sulphuric acid solution and the diazonium solution is warmed, thus giving anthraquinone, fluorenone, and fluorenone-1-carboxylic acid, m. p. 192—193° (cf. Mayer and Freitag, A., 1921, i, 248); the main product of the change, however, is *2′-hydroxybenzophenone-2-carboxylic acid*, colourless needles, m. p. 170—171°, which is converted by methyl sulphate and potassium hydroxide into *2′-methoxybenzophenone-2-carboxylic acid*, colourless crystals, m. p. 144—145°, and by concentrated sulphuric acid into 1-hydroxyanthraquinone, m. p. 191°. H. W.

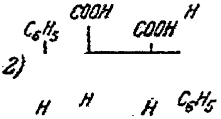
Synthesis of Depsides of *iso*Ferulic Acid [3-Hydroxy-4-methoxycinnamic Acid]. F. MAUTHNER (*J. pr. Chem.*, 1923, **106**, 333—335; cf. A., 1922, i, 936).—*Carbomethoxy*iso*ferulic acid*, obtained by the action of methyl chlorocarbonate on *iso*ferulic acid in alkaline solution, forms crystals, m. p. 223—224° (decomp.). It is converted by phosphorus pentachloride into *carbomethoxy*iso*ferulyl chloride*, colourless needles, m. p. 84°. With *p*-hydroxybenzoic acid, this gives p-*carbomethoxy*iso*ferulyloxybenzoic acid*, colourless crystals, m. p. 206—207°. The carbomethoxy group is removed by the slow action of ammonia in pyridine solution. The depside, p-iso*ferulyloxybenzoic acid*, forms colourless crystals, m. p. 217—218°. m-*Carbomethoxy*iso*ferulyloxybenzoic acid* forms colourless crystals, m. p. 203—204°, and m-iso*ferulyloxybenzoic acid*, colourless crystals, m. p. 191—192°. E. H. R.

Stereoisomerism of the Truxillic Acids and the Discovery of the Remaining Acid of this Group. VIII. R. STOERMER and F. BACHER (*Ber.*, 1924, **57**, [*B*], 15—23).—Theoretically five truxillic acids should exist, the configurations of which are shown by the formulæ:

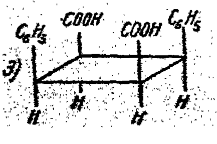
1)



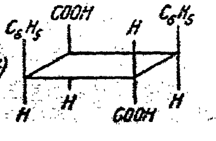
2)



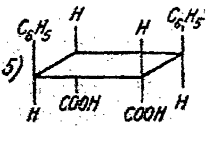
3)



4)



5)

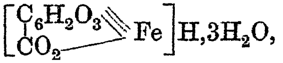


The configurations 1 and 2 have been assigned definitely to α- and γ-truxillic acids respectively (cf. A., 1923, i, 929). ε-Truxillic acid is characterised as a *cis*-compound since it yields a unimolecular, crystalline imide from which it is smoothly regenerated. The *cis*-nature of η-truxillic acid follows from its ready conversion into the anhydride (cf. Stobbe and Zschoch, A., 1923, i, 337); since it is shown that the heavy groups lie on the same side of the *cyclo*butane ring, it is proposed to designate the compound *peri*-truxillic acid (configuration 3). The action of hydrochloric acid at 180° or of an excess of boiling sodium hydroxide on the *peri*-acid yields the outstanding member of the group, which is termed *epi*-truxillic acid owing to its production by a type of epimeric change. The conversion of the *epi*-acid by acetic anhydride into ε-truxillic acid (5) shows it to be a *trans*-compound to which the constitution 4 must necessarily be assigned.

The following individual compounds are described: *peri*-truxillic anhydride, prepared by a modification of the method of Stobbe and Zschoch (*loc. cit.*), m. p. 285°; *peri*-truxillic acid, m. p. 266° (decomp.) (Stobbe and Zschoch give m. p. 280°); *methyl* peri-*truxillate*, obtained by treatment of the acid with an ethereal solution of diazomethane or by the rapid action of methyl sulphate and alkali hydroxide, colourless crystals, m. p. 104—105°; *methyl hydrogen* peri-*truxillate*, from the anhydride and methyl alcohol at 180—200°, m. p. 192°; peri-(? epi-)*truxillamic acid*, small, quadratic plates or needles, m. p. 264° (decomp.); peri-*truxillanilic acid*, m. p. 247° (decomp.), from the *peri*-anhydride and boiling aniline whereby ε-truxilldianilide, m. p. 283°, is also produced; *methyl* peri-*truxillanilate*, m. p. 131°; *methyl* ε-*truxillanilate*, m. p. 159°; epi-*truxillic acid*, prepared most conveniently by heating the *peri*-acid with an excess of sodium hydroxide solution (10%), m. p. 285—287° (with transformation into ε-truxillic acid); *methyl* epi-*truxillate*, from the acid by means of diazomethane, methyl sulphate, or methyl-alcoholic hydrogen chloride, m. p. 111—112°; *methyl hydrogen* epi-*truxillate*, prepared by the partial hydrolysis of the normal ester with alcoholic potassium hydroxide solution, m. p. 204·5°. *epi*-Truxillic acid is converted by aniline at 190—210° into ε-truxilldianilide, and, apparently, a mixture of the two theoretically possible *epi*-truxillanilic acids which has not been separated satisfactorily into its components. H. W.

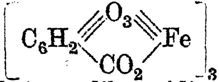
Formation and Ageing of Written Characters. The Primary Ink-salts of Iron Inks. F. ZETZSCHE, G. VIELI, G. LILLJEQVIST, and A. LOOSLI (*Annalen*, 1924, **435**, 233—264).—The primary ink salts have been prepared by the following method: the parent hydroxy compound (*e.g.*, salicylic acid) was treated with the theoretical quantity (see below) of a solution of ferrous sulphate in dilute sulphuric acid, the mixture neutralised with sodium hydroxide, and then shaken in an atmosphere of oxygen and carbon dioxide, until no more oxygen was absorbed. In the case of hydroxy compounds which are readily oxidised in alkaline solution (*e.g.*, pyrogallol), neutralisation was effected in the above oxygen–carbon dioxide atmosphere. In this manner, the formation of the ink salts can be followed and controlled, and that of secondary (oxidation) products avoided. The experimental procedure adopted follows very closely the mechanism of the formation of written characters.

Gallic acid gives rise to *monogallatoferric* acid,

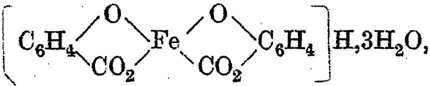


$$\left[\begin{array}{l}C_6H_2O_3 \\ CO_2\end{array} Fe\right]H,3H_2O,$$

a violet, microcrystalline powder, affording gallic acid on being treated with acids, dissolving in alkali to a blue, red, or yellow solution, according to the concentration, the latter solution being oxidised by air to give a yellow substance (galloflavine ?). The conversion of yellow, soluble ferrous gallate, $(C_6H_2[OH]_3\cdot CO_2)_2Fe$, into the above violet compound is reversed in presence of hydrogen and a platinum catalyst.

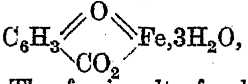
Using a greater proportion of ferrous sulphate to gallic acid, *ferric monogallatoferrate* (?),  $\left[C_6H_2\begin{array}{c}O_3\\CO_2\end{array}Fe\right]_3$ $Fe,12H_2O$, results, as a bluish-violet powder. It is readily oxidised, gives ferric oxide on heating at 85—90° and ferric hydroxide on treating with alkali.

Ferric disalicylate (*disalicylatoferric acid*),



$$\left[C_6H_4\begin{array}{c}O\\CO_2\end{array}Fe\begin{array}{c}O\\CO_2\end{array}C_6H_4\right]H,3H_2O,$$

red needles, gives a bluish-red solution in hot water, carbon dioxide being evolved on boiling. Unless care is taken in the preparation of this compound, Weinland's hexasalicylatotriferridisalicylatoferrate (cf. A., 1917, i, 649, and previous papers) is obtained. Alkali converts the disalicylate into alkali di- and trisalicylatoferrates.

Ferric protocatechuate,  $C_6H_3\begin{array}{c}O\\CO_2\end{array}Fe,3H_2O$, is a violet-blue, microcrystalline powder. The *ferric* salt of gallamide,

$$NH_2\cdot CO\cdot C_6H_2{:}O_3{:}Fe,2\cdot 5H_2O,$$

is a dark blue, microcrystalline powder; the *ferric* salt of gallanilide, $NHPh\cdot CO\cdot C_6H_2{:}O_3{:}Fe,3H_2O$, a dark violet powder and the *ferric* salt of ethyl gallate, $CO_2Et\cdot C_6H_2{:}O_3{:}Fe,2H_2O$, a dark blue powder. The last four compounds give wine-red solutions in aqueous alkali.

The *ferric* salt of tribromopyrogallol, $C_6Br_3{:}O_3{:}Fe,2H_2O$, is a dark blue powder, rapidly becoming brown owing to decomposition. The *diferric* salt of digalloylethyleneglycol,

$$\begin{array}{l}CH_2\cdot O\cdot CO\cdot C_6H_2{:}O_3{:}Fe,2H_2O\\ |\\ CH_2\cdot O\cdot CO\cdot C_6H_2{:}O_3{:}Fe,2H_2O\end{array},$$

is a bluish-violet powder, and the *triferric* salt of trigalloylglycerol, $C_{24}H_{11}O_{15}Fe_3,2H_2O$ (having a constitution similar to that of the glycol derivative) a bluish-violet powder, affording a red solution with alkali. The *pentaferric* salt of pentagalloyl-β-glucose, $C_{41}H_{37}O_{26}Fe_5,10H_2O$, and *pentaferritannate*, $C_{76}H_{37}O_{46}Fe_5,10H_2O$, have similar properties.

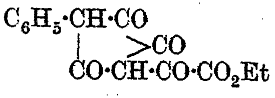
The proportions of phenolic compound to iron (mols. of phenolic compound : atoms of iron) in other primary ferric ink salts (which have not been actually isolated) are as follows: pyrocatechol (violet, 2 : 1), protocatechuic aldehyde (violet, 2 : 1), β-resorcylic acid (reddish-yellow, 1 : 1), gentisic acid (violet-red, 1 : 1), dibromopyrogallol (blue, 1 : 1), dibromogallic acid (dark blue, 1 : 1), and pyrogallolcarboxylic acid (dark violet, 1 : 1).

When ink is applied to paper, neutralisation of the acid present occurs first, followed by atmospheric oxidation of the ferrous salts, which are converted into bluish-violet insoluble primary ink salts (*e.g.*, of the gallic acid type). By the further action of atmospheric oxygen and moisture, the primary salts undergo oxidation, carboxyl or carbethoxyl groups being removed, with formation of carbon dioxide and brown secondary ink salts (*e.g.*, of the pyrogallol type). The black shade acquired by writing ink a week or so after use is due to the presence of a mixture of primary and secondary salts, or, in the case of salts rich in iron, to the presence, also, of ferric hydroxide. The addition of gum arabic to inks hinders atmospheric oxidation and loss of carbon dioxide.

Complete oxidation to the secondary ink salt type takes, on the average, twenty or thirty years. After a much longer time, ferric oxide or hydroxide alone will remain on the paper. E. E. T.

o-Cresoltetrachlorophthalein and some of its Derivatives. E. L. ARNOLD (*J. Amer. Chem. Soc.*, 1924, **46**, 489—493).—*o-Cresoltetrachlorophthalein* was prepared by condensing tetrachlorophthalic acid with *o*-cresol, using stannic chloride. It forms colourless crystals, m. p. 292—293° (decomp.). It resembles phenolphthalein and phenoltetrachlorophthalein, acting as an indicator, purple in alkaline solution; the end-point is between p_H 8·5 and 9. It forms a colourless *diacetyl* derivative, m. p. 207—208°, and a *dimethyl ether*, m. p. 212—213°. In concentrated sulphuric acid it gives a red solution probably due to sulphate formation. The spectrum of *o*-cresoltetrachlorophthalein in absolute ethyl alcohol is very similar to that of phenoltetrachlorophthalein, showing four weak bands in the ultra-violet, whereas that of phenolphthalein has only two bands, which correspond with the more prominent bands of the other two spectra. These bands are of frequency 3523 and 3613. A. B. S.

Ring Syntheses with Ethyl Oxalate. W. WISLICENUS and F. MELMS (*Annalen*, 1924, **436**, 101—112).—Continuing the work of Wislicenus and Schollkopf (A., 1917, i, 700), *ethyl triketophenylcyclopentaneglyoxylate* (annexed formula), was prepared by interaction of benzyl methyl ketone and ethyl oxalate (2 mols.) in presence of potassium ethoxide. This substance (yellow needles, m. p. 169—170°) is strongly enolised. It forms a red *di-potassium* salt and a dark red *copper* salt. The *acid* was obtained by mild alkaline hydrolysis as an orange powder, m. p. 214° (decomp.). When the ester was subjected to acid hydrolysis,



$$\begin{array}{l} C_6H_5\cdot CH\cdot CO \\ \quad\;|\qquad\;\; >CO \\ \quad CO\cdot CH\cdot CO\cdot CO_2Et \end{array}$$

scission took place and 2 : 4 : 5-*triketo*-1-*phenyl*cyclo*pentane* was formed, crystallising from benzene in yellow needles, from alcohol in colourless needles, whilst an orange modification was obtained when the compound was fused and again cooled, or boiled with water. All three forms melted at 167°. An aqueous solution of the substance is strongly acid to litmus and reduces Fehling's solution. The *phenylhydrazone* (only one keto group enters into these reactions) forms greenish-yellow scales, m. p. 241°, the *anil* orange-red scales, m. p. 172°, the p-*toluidine* derivative, red crystals, m. p. 195—196°. The *quinoxaline* formed by interaction with *o*-phenylenediamine forms brown needles, m. p. 251°. The methyl ether, 2 : 4-*diketo-5-methoxy*-1-*phenyl*cyclo*pentene*, in preparing which diazomethane was used, forms colourless crystals, m. p. 54—55°. The *benzylidene* derivative of triketophenyl*cyclo*pentane forms yellow crystals, m. p. 219°; similar derivatives with *p*-tolualdehyde (m. p. 206—207°) and *p*-nitrobenzaldehyde (m. p. 262—264°) were prepared; the latter is noteworthy in that the colour of the solution varies with the solvent employed. The *dibromo* derivative has m. p. 185°. When triketophenyl*cyclo*pentane was dissolved in alkali and reprecipitated, it was found to have been converted apparently into a *bis*-product of high melting point. A preliminary investigation of the condensations of ethyl β-ethoxyglutaconate, ethyl acetonedicarboxylate, and ethyl acetoacetate is described. W. A. S.

Polymorphic Forms and Thermotropic Properties of Schiff's Bases derived from 5-Iodo-4-hydroxy-3-methoxybenzaldehyde. R. M. Hann (*J. Washington Acad. Sci.*, 1924, **14**, 79—86).—Derivatives of the Schiff base type have been prepared from 5-iodo-4-hydroxy-3-methoxybenzaldehyde and aromatic amines. These 5-iodovanillidene compounds are not phototropic, but on vigorous trituration they change colour owing to the production of polymorphic forms. The introduction of iodine into *p*-hydroxy-*m*-methoxybenzaldehyde results in the disappearance of the power to undergo thermotropic change in the vanillidene derivatives. The following compounds are described: 5-*iodovanillideneaniline*, deep red bipyramids, changing to an orange powder, m. p. 152—153°; 5-*iodovanillidene*-o-*chloroaniline*, yellowish-brown crystals, m. p. 143°; 5-*iodovanillidene*-p-*chloroaniline*, red needles, changing to an orange powder, m. p. 110—111° (decomp.); 5-*iodovanillidene*-p-*bromoaniline*, yellowish-brown powder, changing to yellowish-green, with metallic lustre, m. p. 108° (partial decomp.); 5-*iodovanillidene*-p-*iodoaniline*, yellowish-brown powder, changing to yellowish-green with metallic lustre, m. p. 98°; 5-*iodovanillidene*-o-*toluidine*, light yellow needles, changing to deep yellow, m. p. 120—121°; 5-*iodovanillidene*-m-*toluidine*, orange-red granules, darkening on trituration, m. p. 103—104°; 5-*iodovanillidene*-p-*toluidine*, brilliant golden-yellow crystals, becoming nearly colourless on trituration, m. p. 160—161°; 5-*iodovanillidene*-α-*naphthylamine*, yellowish-brown crystals, changing to bright yellow, decomposes at 226°; 5-*iodovanillidene*-β-*naphthyl-*

amine, light yellow needles, changing to deep yellow, m. p. 163°; 5-*iodovanillidene-ψ-cumidine*, chocolate-brown powder, changing to yellow, m. p. 165°; 5-*iodovanillidenebenzidine*,

$C_6H_4I(OMe)(OH)\cdot CH:N\cdot C_6H_4\cdot C_6H_4\cdot NH_2$,

bright orange flocks, crimson on trituration, m. p. 160—161° (incipient decomp.). R. B.

o-Methoxydiphenylacetaldehyde and its Transformations. R. STOERMER and F. FRICK (*Ber.*, 1924, **57**, [*B*], 23—29).—αα-o-*Methoxydiphenylethylene glycol*, $MeO\cdot C_6H_4\cdot CPh(OH)\cdot CH_2\cdot OH$, long needles, m. p. 96°, prepared in moderate yield by the action of magnesium *o*-anisyl bromide on benzoylcarbinol, is smoothly converted by hot sodium hydrogen sulphite solution into o-*methoxydiphenylacetaldehyde*, a viscous liquid, b. p. 198°/16 mm.; the corresponding *semicarbazone* has m. p. 175°, whereas an oxime or a phenylhydrazone could not be isolated. The aldehyde is converted by glacial acetic and hydrobromic acids into 1-phenylcoumarone, m. p. 120°, instead of the expected 2-phenyl derivative. Probably the migration of the phenyl group takes place in an intermediately formed tolane derivative which could not be isolated. The aldehyde is transformed by phosphorus pentachloride into α-*chloro*-ββ-o-*methoxydiphenylethylene*, b. p. 190°/11 mm., which, however, is converted by sodium ethoxide at 200° immediately into 1-phenylcoumarone.

o-Methoxydiphenylacetaldehyde is decomposed by an excess of alcoholic potassium hydroxide solution at 180—200° into potassium formate and o-*methoxydiphenylmethane*, long, colourless needles, m. p. 30°, the constitution of which is established by its formation from *o*-methoxybenzophenone by Clemmensen's method; the corresponding *phenylurethane* has m. p. 115°. The methoxy derivative is converted by glacial acetic and hydrobromic acids at 150° into o-*hydroxydiphenylmethane*, b. p. 175°/18 mm., m. p. 15°.

The aldehyde is oxidised in acetone solution by potassium permanganate in the presence of potassium carbonate to o-*methoxydiphenylacetic acid*, m. p. 125°; it is reduced by aluminium amalgam in the presence of moist ether to o-*methoxydiphenylethyl alcohol*, a colourless, very viscous liquid, b. p. 220°/30 mm. (*phenylurethane*, m. p. 107°; *benzoate*, m. p. 98°), which is converted by acetic and hydrobromic acids into 2-phenylcoumaran, m. p. 39°, together with much resinous matter.

as-o-*Methoxydiphenylethylene oxide*, m. p. 90°, is obtained as a by-product of the preparation of αα-*o*-methoxydiphenylethylene glycol; it is transformed by dilute hydrochloric acid at 180° into methoxydiphenylacetaldehyde. H. W.

Action of Piperidine on Phenyl α-Bromostyryl Ketone. Production of a New Ketone, Phenylbenzylglyoxal. C. DUFRAISSE and H. MOUREU (*Compt. rend.*, 1924, **178**, 573—575; cf. A., 1922, i, 843; 1923, i, 113).—Piperidine converts phenyl α-bromostyryl ketone into *phenyl α-bromo-β-phenyl-α-piperidinoethyl ketone*, $COPh\cdot CBr(NC_5H_{10})\cdot CH_2Ph$, a pale yellow, sparingly soluble substance, m. p. 164°, very unstable, but forming stable salts with acids. This ketone, with 1 mol. of alkali in alcoholic solution, affords the red piperidinobenzylideneacetophenone described by Watson (T., 1904, **85**, 1322) and now shown to be phenyl α-piperidinostyryl ketone, $COPh\cdot C(NC_5H_{10}){:}CHPh$. The latter substance, on hydrolysis by acid, is converted into *phenylbenzylglyoxal*, $Bz\cdot CO\cdot CH_2Ph$, a pale yellow solid, m. p. 67—68°, unstable in air, but stable in a vacuum. E. E. T.

Additive Compounds of Metallic Salts and Doubly Unsaturated Aromatic Ketones. W. DILTHEY and O. RAUCHHAUPT (*Ber.*, 1924, **57**, [*B*], 309—310).—Concentrated solutions of di-*p*-methoxystyryl ketone and ferric chloride in glacial acetic acid yield the additive *compound*, $[(OMe\cdot C_6H_4\cdot CH{:}CH)_2CO]_2,FeCl_3$, dark violet needles, m. p. 146° after previous decomposition. In a similar manner, o-*chlorostyryl methoxystyryl ketone*, yellow crystals, m. p. 109°, gives the *compound*, $C_{36}H_{30}O_2Cl_4Fe$, dark violet needles, m. p. 155—156° (decomp.). Uranyl chloride and distyryl ketone yield the product, $[(CHPh{:}CH)_2CO]_2,UO_2Cl_2$, small, golden-yellow leaflets, m. p. 264° after incipient decomposition at 200°; the corresponding *compound*, $C_{38}H_{36}O_8Cl_2U$, from di-*p*-methoxystyryl ketone, crystallises in violet-red, hexagonal leaflets, m. p. about 258° (incipient decomp. 150°). The additive *compound*, $[(C_6H_4[OMe]\cdot CH{:}CH)_2CO]_2,VCl_2$, brownish-yellow needles, is prepared from its components dissolved in glacial acetic acid.
H. W.

Synthesis of Nitranilic Acid. H. O. MEYER (*Ber.*, 1924, **57**, [*B*], 326—328).—Nitranilic acid [3 : 6-dinitro-2 : 5-dihydroxy-*p*-benzoquinone] is obtained in 72—78% yield by the action of fuming nitric acid (*d* 1·459) on *p*-benzoquinone at −5° to −10°. It crystallises in lemon-yellow needles, m. p. 86—87°, whereas Nietzki (A., 1911, i, 69) gives m. p. 100°. The potassium salt, $C_6O_8N_2K_2$, exists in two distinct crystalline forms. The *rubidium* salt, $C_6O_8N_2Rb_2$, yellow needles, is described. H. W.

Action of Potassium Ferricyanide on Purpurin in Alkaline Solution. R. SCHOLL and P. DAHLL (*Ber.*, 1924, **57**, [*B*], 80—83).—Purpurin is readily oxidised in alkaline solution by potassium ferricyanide at the atmospheric temperature to *o*-phthalic acid and 2 : 5-dihydroxy-*p*-benzoquinone, *o*-2 : 5-dihydroxy-*p*-benzoquinonoylbenzoic acid being apparently produced initially. The first stage of the oxidation of purpurin is therefore similar to that of alizarin (Scholl and Zinke, A., 1919, i, 25; 1920, i, 169) and quinizarin (this vol., i, 178). Dihydroxyanthraquinones which contain the hydroxy group attached to different nuclei and monohydroxyanthraquinones are not affected by potassium ferricyanide in alkaline solution at the atmospheric temperature. The hypothesis that oxidative fission occurs through the diquinones therefore receives further support.

In addition to the orange-yellow modification described in the literature, 2 : 5-dihydroxy-*p*-benzoquinone exists in a pale yellow, metastable *modification* which is stable only in the presence of acetic acid. The substance is readily converted by methyl-alcoholic hydrogen chloride into the dimethyl ether. H. W.

Dyestuffs of the Phenanthrene Series. K. Brass (*Z. angew. Chem.*, 1924, **37**, 67—69).—Phenanthraquinonyl azides behave in a similar manner to phenyl azides towards sulphuric acid. Thus, 2-azidophenanthraquinone yields 2-amino-3-hydroxyphenanthraquinone, from which 2 : 3-dihydroxyphenanthraquinone is prepared in the usual manner, some 2-aminophenanthraquinone being formed at the same time. Under certain conditions 4-azidophenanthraquinone yields, with sulphuric acid, 4-amino-1-hydroxyphenanthraquinone, and under others 1 : 4-dihydroxyphenanthraquinone. These compounds are dyestuffs for wool and cotton. The presence of a hydroxyl group in the *o*-position to an amino- or a hydroxyl group has little or no effect on the tinctorial properties of the parent compounds, whereas its presence in the *p*-position to such groups greatly enhances their value. As mordant dyestuffs the 4-amino-1-hydroxy and 1 : 4-dihydroxy compounds are more powerful than the 2-amino-3-hydroxy and 2 : 3-dihydroxy compounds. The simple aminophenanthraquinones are also dyestuffs for wool, and possess more powerful tinctorial properties than the simple aminoanthraquinones. [Cf. *B.*, 1924, 246.]
W. T. K. B.

Azido-, Aminohydroxy-, and Dihydroxy-phenanthraquinones. I. K. Brass, E. Ferber, and J. Stadler (*Ber.*, 1924, **57**, [*B*], 121—128).—2-Aminophenanthraquinone behaves as an amine of the benzene series, in which the basic character is repressed by the presence of acidic groups; its diazotisation and the conversion of its diazonium hydrogen sulphate into a series of derivatives are described.

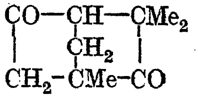
2-Aminophenanthraquinone is conveniently diazotised in accordance with the method of Schmidt and Soll (A., 1908, i, 996), somewhat less advantageously in the presence of concentrated sulphuric acid. *Phenanthraquinone-2-diazonium perbromide*, $C_{14}H_7O_2N_2Br_3$, orange-yellow crystals which lose bromine at the atmospheric temperature, is prepared by treating a solution of the diazonium sulphate with an excess of bromine dissolved in potassium bromide solution. It is transformed by ice-cold ammonia solution (25%) into 2-*azidophenanthraquinone*, cinnabar-red leaflets, m. p. 186° (decomp.) after darkening at 175°, which is converted by *o*-phenylenediamine hydrochloride into 2-*azidophenanthraphenazine*, $C_{20}H_{11}N_5$, long, yellow needles, m. p. 190° (decomp.) after softening at 180°. The action of sulphuric acid on the azide gives a mixture of 2-aminophenanthraquinone and 2-*amino*-3-*hydroxyphenanthraquinone*, bluish-black needles, which softens at 120°, but does not melt in a capillary tube at a higher temperature. The mixture of products yields phthalic acid when oxidised. 2 : 3-*Dihydroxyphenanthraquinone*, prepared by diazotisation of the hydroxy-amine in concentrated sulphuric acid solution, crystallises in slender, reddish-brown needles which have no definite melting point; it yields a *mono-sodium* salt and a *quinoxaline* derivative, small, orange-yellow needles, m. p. 162° (decomp.). H. W.

Azido-, Aminohydroxy-, and Dihydroxy-phenanthraquinones. II. K. Brass and J. Stadler (*Ber.*, 1924, **57**, [*B*], 128—136).—4-Aminophenanthraquinone is converted by sodium nitrite in the presence of concentrated sulphuric acid into the corresponding diazonium salt, which is relatively unstable in comparison with phenanthraquinone-2-diazonium sulphate (preceding abstract). It is transformed by a solution of bromine in concentrated potassium bromide solution into *phenanthraquinone*-4-*diazonium perbromide*, an orange-red, crystalline powder, from which 4-*azidophenanthraquinone*, red needles, is obtained by the action of aqueous ammonia (10%). 4-*Azidophenanthraphenazine*, prepared from the azide and *o*-phenylenediamine hydrochloride, crystallises in slender, yellow needles, m. p. 197° (decomp.). 4-Azidophenanthraquinone reacts with dilute sulphuric acid with unexpected ease, and after prolonged treatment at the temperature of boiling water yields solely 1 : 4-*dihydroxyphenanthraquinone*, very slender, bluish-violet needles (1 : 4-*diacetoxyphenanthraquinone*, prisms, m. p. 183°; 1 : 4-*dihydroxyphenanthraphenazine*, brownish-red, lustrous needles, m. p. 288°). The attachment of the two hydroxy groups to the same benzene nucleus is established by the observation that phthalic acid is the only isolable product of its oxidation. The compound must therefore be either 1 : 4- or 3 : 4-dihydroxyphenanthraquinone, and, since the latter constitution has already been assigned to morpholquinone, from which the present compound is quite distinct, the former alternative is selected. It appears, however, to be quite exceptional for a substituent to enter the phenanthraquinone nucleus in the 1-position. Oxidation of 1 : 4-dihydroxyphenanthraquinone in ethereal solution with silver oxide or lead tetra-acetate leads to the formation of a yellow op-*diquinone* which has not been isolated in the homogeneous condition.

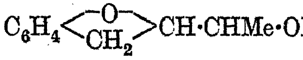
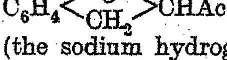
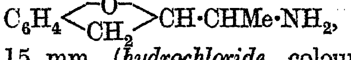
4-*Amino*-1-*hydroxyphenanthraquinone* is prepared by the action of sulphuric acid on the azide at a temperature not exceeding 90°. It crystallises in violet-black aggregates of needles, decomp. 218° after subliming at 165°. The *sulphate* and the *hydrochloride* are described; the *sodium* salt is hydrolysed by water. It is transformed by hot, dilute sulphuric acid into 1 : 4-dihydroxyphenanthraquinone. H. W.

Formation of Diketocamphane (Ketocamphor) and of Diketofenchane (Ketofenchone) by the Oxidation of Camphor and Fenchone with Chromic Acid. J. Bredt (*J. pr. Chem.*, 1923, **106**, 336—347).—The *p*-diketocamphane described by Bredt and Goeb (A., 1921, i, 257) has now been obtained by the oxidation of both natural and inactive synthetic camphor with chromic acid. The product in both cases melts at 210° and the yield is only 4—5% of the theoretical. In its physiological action, *p*-diketocamphane is similar to camphor, and it has the advantage of greater solubility in water.

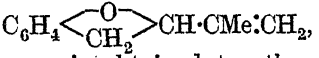
By oxidation of fenchone in glacial acetic acid solution with chromic acid below 15° (the reaction takes about 5 weeks), *ketofenchone* is obtained, probably having the annexed formula. It forms long, thin needles, m. p. 42·5—43°, has a typical lactone odour, and is readily volatile in steam; b. p. 108°/10·5 mm. The new keto group is more active than the original keto group of fenchone, and there are readily formed a *monophenylhydrazone*, white needles, m. p. 149—150° (decomp.), and a *monosemicarbazone*, thin needles, m. p. 222—223°. Ketofenchone has $[\alpha]_D^{21}$ +75·78° in benzene. E. H. R.



Solubility of Sulphur in Caoutchouc. W. J. KELLY and K. B. AYERS (*Ind. Eng. Chem.*, 1924, **16**, 148—150).—The distribution of dissolved sulphur between unvulcanised rubber and amyl or *n*-butyl alcohol obeys Henry's law. The sulphur consequently is present in the rubber in a state of solution and not of adsorption. For the determination of the solubility of sulphur in rubber it is convenient to suspend strips of the latter in a saturated solution of sulphur in butyl alcohol in the presence of solid sulphur; when equilibrium is attained, the dissolved sulphur is extracted from the rubber with acetone and its amount determined. [Cf. *B.*, 1924, 266.] D. F. T.

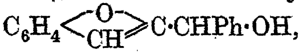
Reduction Products of 1-Acylcoumarones. R. STOERMER, C. W. CHYDENIUS, and E. SCHINN (*Ber.*, 1924, **57**, [*B*], 72—80).—1-Acetylcoumarone, b. p. 136°/11 mm., m. p. 76° (cf. Stoermer and Schäffer, A., 1903, i, 846), is prepared conveniently by the action of chloroacetone on salicylaldehyde and potassium hydroxide dissolved in alcohol; the *phenylhydrazone*, pale yellow crystals, m. p. 153—154°, and the *semicarbazone*, colourless needles, m. p. 217°, are described. Reduction of the ketone by sodium amalgam in the presence of alcohol acidified with acetic acid yields coumaranylmethylcarbinol,  $C_6H_4\genfrac{<}{>}{0pt}{}{O}{CH_2}CH{\cdot}CHMe{\cdot}OH$, and *acetylcoumarane*,  $C_6H_4\genfrac{<}{>}{0pt}{}{O}{CH_2}CHAc$, a colourless liquid, b. p. 132—133°/12 mm. (the sodium hydrogen sulphite *compound*, the *oxime*, m. p. 111—112°, the *phenylhydrazone*, yellow leaflets, m. p. 113°, and the *semicarbazone*, m. p. 192°, are described). *Diacetylbiscoumarane*, $C_{20}H_{18}O_4$, m. p. 183°, gives a *mono-oxime*, m. p. 177°. Reduction of acetylcoumaraneoxime by sodium amalgam and alcohol leads to the formation of small quantities of 1-*α-aminoethylcoumarane*,  $C_6H_4\genfrac{<}{>}{0pt}{}{O}{CH_2}CH{\cdot}CHMe{\cdot}NH_2$, a fairly mobile liquid, b. p. 153°/15 mm. (*hydrochloride*, colourless, lustrous leaflets, m. p. 117—118°; *picrate*, yellow leaflets, decomp. 209°).

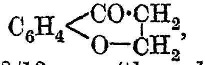
Reduction of acetylcoumarone with sodium and alcohol according to the method of Stoermer and Schäffer (*loc. cit.*) gives acetylcoumarane, coumaranylmethylcarbinol, and *o*-hydroxyphenylbutan-γ-ol, m. p. 66—67°; the latter substance may also be obtained by reduction of coumaranylmethylcarbinol. It is converted by bromine in chloroform solution into 4-*bromo*-2-*hydroxyphenylbutan*-γ-*ol*, long, colourless needles, m. p. 94—95°. o-*Methoxyphenylbutan*-γ-*ol*, a colourless, viscous liquid, b. p. 143°/12 mm., is prepared by the action of methyl iodide and potassium hydroxide on an alcoholic solution of the corresponding phenol. It is converted by zinc chloride at 150° into *o*-Δ^{β}-butenylanisole, b. p. 104—106°/12 mm., d_4^{19} 0·9721, n_D^{19} 1·5255 (cf. von Braun and Schirmacher, A., 1923, i, 286), which is isomerised when heated with a small quantity of potash-lime to o-Δ^{α}-*butenylanisole*, b. p. 106—108°/12 mm., d_4^{18} 0·9819, n_D^{18} 1·5346.

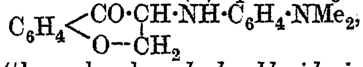
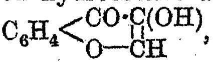
1-iso*Propenylcoumarane*,  $C_6H_4{<}\substack{O\\CH_2}{>}CH\cdot CMe{:}CH_2$, a mobile liquid, b. p. 106—108°/12 mm., is obtained together with much resinous matter by the action of magnesium methyl iodide on acetylcoumarane.

1-Benzoylcoumarone, m. p. 90—91° (*semicarbazone*, m. p. 137°), is conveniently obtained by the action of bromoacetophenone and potassium hydroxide on salicylaldehyde in alcoholic solution. Somewhat unexpectedly, it is reduced by sodium and alcohol mainly to 1-*benzylcoumarane*, m. p. 26°, b. p. 185°/15 mm.; small quantities of β-o-*hydroxyphenylethylphenylcarbinol*,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CHPh\cdot OH,$$

slender needles, m. p. 94° (*phenylurethane*, m. p. 124°; *diphenylurethane*, m. p. 52°), are simultaneously produced. *Coumaronylphenylcarbinol*,  $C_6H_4{<}\substack{O\\CH}{\geqslant}C\cdot CHPh\cdot OH$, m. p. 76°, is obtained by the reduction of benzoylcoumarone with sodium amalgam in acid-alcoholic solution at the atmospheric temperature; the corresponding *phenylurethane* has m. p. 126°. *Benzoylcoumarone-oxime*, m. p. 132°, is reduced by sodium amalgam in faintly acid, alcoholic solution to *coumaronylphenylaminomethane*, a colourless liquid, b. p. 200°/11 mm. (*hydrochloride*, m. p. 210°). It is converted by one molecular proportion of sodium nitrite into coumarylphenylcarbinol and by two molecular proportions into benzoylcoumarone; it is reduced by sodium and alcohol to benzoylcoumarane. 1-*Benzylcoumarone*, b. p. 180—185°/15 mm., cannot be prepared from the benzoyl compound by Clemmensen's method, but is obtained when the hydrazone is heated with an alcoholic solution of sodium ethoxide at 220—230°. Attempts to prepare it by converting coumarylphenylcarbinol by means of thionyl chloride into coumarylphenylmethyl chloride and reduction of the latter substance with zinc dust and acetic acid yielded a *compound*, $C_{30}H_{26}O_2$, m. p. 98°, probably 1 : 1′-dibenzyl-2 : 2′-dicoumarane. H. W.

Synthesis of 4-Ketochroman [Chromanone]. F. MAYER and L. VAN ZÜTPHEN (*Ber.*, 1924, **57**, [*B*], 200—202; cf. Arndt and Källner; Krollpfeiffer and Schultze, succeeding abstracts).—β-Chloropropionyl chloride is converted by phenol in the presence of carbon disulphide and aluminium chloride or phosphoryl chloride into a mixture of phenyl β-chloropropionate, b. p. 132—135°/12 mm., and a *substance*, $C_9H_{10}O_3$, m. p. 141—142°, which is regarded provisionally as *o*(?*p*)-hydroxyphenyl β-hydroxyethyl ketone. The ester is transformed by aluminium chloride into o-*hydroxyphenyl β-chloroethyl ketone*, colourless prisms, m. p. 70°, and p-*hydroxyphenyl β-chloroethyl ketone*, colourless, lustrous leaflets, m. p. 90° (m. p. 75—80°, directly after crystallisation from water), which are separated from one another by distillation with steam, with which only the ortho-derivative is volatile; the compound $C_9H_{10}O_3$ (above) is also formed in small amount. The ortho-compound is converted by aluminium chloride at 160—180° into 4-*ketochroman* [*chromanone*],  $C_6H_4{<}\begin{array}{l}CO\cdot CH_2\\ \quad\;\,|\\ O-CH_2\end{array}$, colourless, slender needles, m. p. 111°, b. p. 128°/13 mm. (the *sodium* salt, yellow crystals, the *oxime*, long, colourless needles, m. p. 144—145°, and the *benzylidene* derivative, m. p. 147—150°, are described). H. W.

Chromanone and Chromonol. F. Arndt and G. Källner (*Ber.*, 1924, 57, [*B*], 202—206; cf. Mayer and van Zütphen, preceding abstract; Krollpfeiffer and Schultze, succeeding abstract).—β-Phenoxypropionic acid is converted by concentrated sulphuric acid or, more advantageously from the point of view of yield, by successive treatment with phosphorus pentachloride and aluminium chloride in the presence of benzene, into *chromanone*, colourless plates, b. p. 127—128°/13 mm., m. p. 38° (Mayer and van Zütphen, *loc. cit.*, give m. p. 111°); 3-*benzylidenechromanone*, almost colourless crystals, has m. p. 113° (Mayer and van Zütphen give m. p. 147—150°). Chromanone condenses with *p*-nitrosodimethylaniline in alcoholic solution in the presence of potassium hydroxide and the product is reduced by hydrazobenzene to (?)3-p-*dimethylaminophenylaminochromanone*,  $C_6H_4{<}\begin{array}{l}CO\cdot CH\cdot NH\cdot C_6H_4\cdot NMe_2\\ \quad\;\,|\\ O-CH_2\end{array}$, golden-yellow leaflets, m. p. 154° (the colourless *hydrochloride* is described), which is oxidised by potassium ferricyanide to the corresponding, very unstable anil. The latter substance is converted by boiling, concentrated hydrochloric acid into *chromonol* (3-*hydroxy*-1 : 4-*benzopyrone*),  $C_6H_4{<}\begin{array}{l}CO\cdot C(OH)\\ \quad\;\,\|\\ O-CH\end{array}$, coarse, colourless needles, m. p. 181°; the *sodium*, *calcium*, and *magnesium* derivatives are described. The *benzoate* crystallises in colourless needles, m. p. 177·5°. 3-*Bromochromanone* has m. p. 69—70°. H. W.

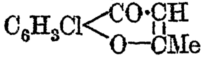
Ring Closures from β-Phenoxypropionic Acids to Chromanones. F. Krollpfeiffer and H. Schultze (*Ber.*, 1924, 57, [*B*], 206—207; cf. Mayer and van Zütphen; Arndt and Källner, preceding abstracts).—The formation of chromanones from β-phenoxyphenylpropionic acids is most conveniently effected by heating mixtures of the latter and phosphoric anhydride under diminished pressure; the action of concentrated sulphuric acid or of phosphoric oxide in the presence of benzene is less suitable. *Chromanone* crystallises in colourless leaflets, m. p. 39—40°, b. p.

124°/14 mm.; the *semicarbazone*, small, colourless needles, has m. p. 227°. β-p-*Toloxypropionic acid*, colourless needles, m. p. 147—148°, yields 6-methylchromanone, m. p. 34—36° (cf. von Auwers and Krollpfeiffer, A., 1915, i, 442). H. W.

Syntheses of Chromones and Coumarins. G. WITTIG (*Ber.*, 1924, **57**, [*B*], 88—95).—Chromones are readily obtained by condensation of *o*-acetylphenols with sodium and ethyl acetate, followed by ring closure of the diketones thus produced.

The displacement of the acetyl group into the ortho position to the hydroxy radical is effected by heating the phenolic esters with aluminium chloride at 110—115°; 4-chloro-6-acetylphenol (3-chloro-6-hydroxyphenyl methyl ketone), m. p. 53·5—54·7°, 4-*chloro*-6-*acetyl*-m-*cresol*, colourless needles, m. p. 69—70°, and 6-acetyl-*p*-cresol, m. p. 45—46°, are described.

4-Chloro-6-acetylphenol is converted by acetic anhydride and sodium acetate at 160—170° into a mixture of 6-chloro-4-methylcoumarin, m. p. 186—187°, and 6-*chloro*-2-*methylchromone*,



$C_6H_3Cl<\begin{matrix}CO\cdot CH\\ \quad\;\; \| \\ O—CMe\end{matrix}$, colourless needles, m. p. 115—116°. The substances are separated from one another by means of an alcoholic solution of sodium ethoxide, which causes fission of both rings with the production of 5-*chloro*-β-*methylcoumaric acid*, m. p. 156° (decomp.), and 4-chloro-6-acetylacetophenol. Addition of acid converts the former into its lactone, whereas the latter can be removed by aqueous sodium hydroxide and subsequently reconverted into its cyclic compound by sulphuric acid. The mixture of chromone and coumarone is converted by boiling 2*N*-sodium hydroxide solution into 5-chlorosalicylic acid, m. p. 173—174°, which owes its formation to fission of the intermediately formed diketone, $OH\cdot C_6H_3Cl\cdot CO\cdot CH_2\cdot COMe$.

A similar series of reactions has been applied to 4-chloro-6-acetyl-*m*-cresol, whereby the following compounds are produced: 6-*chloro*-4 : 7-*dimethylcoumarin*, needles, m. p. 206—207°; 4-*chloro*-6-*acetylaceto*-m-*cresol*, pale yellow, lustrous leaflets, m. p. 115·5—116·5°; 6-*chloro*-2 : 7-*dimethylchromone*, needles, m. p. 144·5—145·5°; 5-chloro-4-methylsalicylic acid, m. p. 203—204°. Similarly, 6-acetyl-*p*-cresol gives 2 : 6-dimethylchromone, m. p. 99·5—100°, 4 : 6-dimethylcoumarin, m. p. 147·5—148°, and 5-methylsalicylic acid, m. p. 148·5—149°.

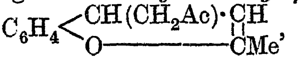
p-Chlorophenyl methyl ether is converted by acetyl chloride and aluminium chloride in the presence of carbon disulphide into 4-*chloro*-6-*acetylphenyl methyl ether*, needles, m. p. 29—30°, which is transformed by sodium and ethyl acetate into 4-*chloro*-6-*acetylacetophenyl methyl ether*, yellow prisms, m. p. 76·5—77·5°; the latter compound is converted by concentrated hydriodic acid or, less advantageously, by hydrobromic and glacial acetic acids into 6-chloro-2-methylchromone.

The preparation of 6-chloro-2-methylchromone, 6-chloro-2 : 7-dimethylchromone, and 2 : 6-dimethylchromone by the action of sodium and ethyl acetate on the requisite phenol is described.

4-*Chloro*-6-*acetylacetophenol* crystallises in pale yellow leaflets, m. p. 110—111°; 6-*acetylaceto*-p-*cresol* has m. p. 94·5—96°.

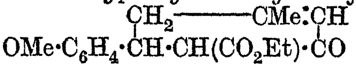
H. W.

Interaction of Ethyl Acetoacetate with o-Hydroxystyryl Ketones. T. A. Forster and I. M. Heilbron (*J. Chem. Soc.*, 1924, **125**, 340—347).—2-Hydroxystyryl methyl ketone condenses with ethyl acetoacetate, in presence of sodium ethoxide or aqueous sodium hydroxide, to give 4-*acetonyl*-2-*methyl*-γ-*pyran*,



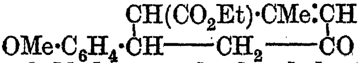
$$C_6H_4<\begin{matrix}CH(CH_2Ac)\cdot CH\\ O\text{————}CMe\end{matrix},$$

colourless needles, m. p. 134—135° (*phenylhydrazone*, colourless needles, m. p. 200°). Condensation of 2-hydroxystyryl phenyl ketone with ethyl benzoylacetate similarly affords 2-*phenyl*-4-*phenacyl*-γ-*pyran*, colourless crystals, m. p. 130°, together with 2-*phenyl*-4-*phenacyl*-γ-*pyran*-3-*carboxylic acid*, colourless prisms, m. p. 157°. Condensation of 2-methoxystyryl methyl ketone with ethyl acetoacetate affords *ethyl* 3-o-*methoxyphenyl*-5-*methyl*-Δ⁵-cyclo*hexen*-1-*one*-2(or 4)-*carboxylate*,



$$\begin{matrix}CH_2\text{———}CMe{:}CH\\ OMe\cdot C_6H_4\cdot CH\cdot CH(CO_2Et)\cdot CO\end{matrix}$$

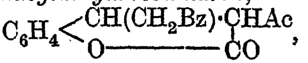
or



$$\begin{matrix}CH(CO_2Et)\cdot CMe{:}CH\\ OMe\cdot C_6H_4\cdot CH\text{——}CH_2\text{——}CO\end{matrix},$$

pale yellow needles, m. p. 139°.

2-*Methoxystyryl phenyl ketone* (colourless needles, m. p. 60°) condenses with ethyl acetoacetate to give *ethyl* 5-*phenyl*-3-o-*methoxyphenyl*-Δ⁵-cyclo*hexen*-1-*one*-2-*carboxylate*, colourless prisms, m. p. 95°, whilst 2-hydroxystyryl phenyl ketone under similar conditions affords 3-*acetyl*-4-*phenacyldihydrocoumarin*,



$$C_6H_4<\begin{matrix}CH(CH_2Bz)\cdot CHAc\\ O\text{————}CO\end{matrix},$$

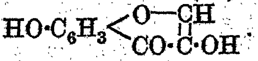
colourless needles, m. p. 175°, together with a small quantity of a colourless crystalline *substance*, m. p. 214°.

6-, 7-, and 8-*Methoxy*-4-*acetonyl*-2-*methyl*-γ-*pyran* respectively form feathery needles, m. p. 119°, colourless crystals, m. p. 149°, and colourless needles, m. p. 168°, the 8-compound affording a colourless, crystalline *phenylhydrazone*, m. p. 186°.

Spectrographic measurements support certain of the above constitutional formulæ.

F. G. W.

The Brazilin and Hæmatoxylin Question. III. The Degradation Product of Brazilin obtained by Schall and Dralle. P. Pfeiffer and J. Oberlin (*Ber.*, 1924, **57**, [*B*], 208—213; cf. A., 1917, i, 661; 1920, i, 561).—The compound, $C_9H_6O_4$, isolated by Schall and Dralle (A., 1892, 502) by the action of atmospheric oxygen on an alkaline solution of brazilin has been considered by Feuerstein and von Kostanecki (A., 1899, i, 538) to be 3 : 7-dihydroxychromone,



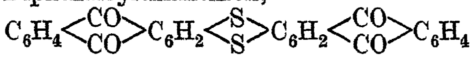
$$HO\cdot C_6H_3<\begin{matrix}O\text{—}CH\\ CO\cdot C\cdot OH\end{matrix}.$$

This is confirmed by the observation that synthetic 3 : 7-dimethoxychromone is identical with the dimethyl ether of the degradation product.

β-3-*Methoxyphenoxypropionic acid*, $OMe\cdot C_6H_4\cdot O\cdot CH_2\cdot CH_2\cdot CO_2H$, colourless, lustrous crystals, m. p. 81—83°, is prepared in poor yield (17%) from resorcinol methyl ether and β-iodopropionic acid. It is converted by treatment with zinc chloride at 145°, with phosphoric anhydride at about 100°, or by the successive action of phosphorus pentachloride and aluminium chloride, into 7-methoxychromanone, identical with the product obtained by Pfeiffer and Grimmer by the reduction of 7-methoxychromone (cf. A., 1917, i, 661). The chromanone is transformed by amyl nitrite and potassium amoxide in amyl alcoholic solution into 3-*oximino-7-methoxychromanone* (3-*oximino*-7-*methoxy*-2 : 3-*dihydro*-1 : 4-*benzopyrone*), almost colourless, microscopic leaflets, m. p. 146—147° (decomp.), which, when treated with glacial acetic and dilute sulphuric acids, gives 3-*hydroxy*-7-*methoxychromone* (3-*hydroxy*-7-*methoxy*-1 : 4-*benzopyrone*), colourless, microscopic needles, m. p. 171—172°. 3 : 7-*Dimethoxychromone*, prepared from the preceding compound and methyl sulphate, forms colourless crystals, m. p. 169—170°. H. W.

Linear and Angular Diphthaloylthianthrens. K. Brass and K. Heide (*Ber.*, 1924, **57**, [*B*], 104—121).—An extension of the work on compounds containing the dithiin ring to anthracene derivatives. In these, the stability of the ring is much greater than in the corresponding naphthalene compounds (cf. Brass and Köhler, A., 1922, i, 1050), and its conversion by loss of an atom of sulphur into the thiophen ring is effected only under drastic conditions. Contrary to the views of Scholl and Seer (A., 1911, i, 557), both linear and angular diphthaloylthianthrens are well-defined vat dyes.

2 : 3 : 6 : 7-Diphthaloylthianthren,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{S}{S}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_4$$

(cf. Scholl and Seer, *loc. cit.*), is prepared by heating a mixture of molecular proportions of 2 : 3-dibromoanthraquinone and crystalline sodium sulphide gradually to 210° under pressure; it crystallises in small, brown needles which do not melt below 360°. It is remarkably stable towards nitric acid. It is reduced by alkaline sodium hyposulphite or by zinc dust and alkali hydroxide to *tetrahydroxydinaphthathianthren*, pale greenish-yellow needles; the *tetrabenzoate*, golden-yellow needles, which darken at 320° but do not melt below 350°, is hydrolysed and oxidised by concentrated sulphuric acid to benzoic acid and diphthaloylthianthren.

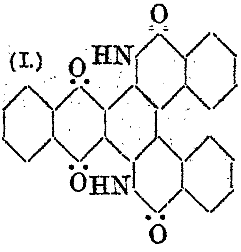
2 : 3-Dibromoquinizarin is transformed by boiling acetic anhydride in the presence of fused zinc chloride into the corresponding *diacetate*, pale yellow needles, m. p. 242° (indefinite), and by benzoyl chloride in the presence of nitrobenzene into the *dibenzoate*, yellow needles. It is converted by an equimolecular proportion of crystalline sodium sulphide at a temperature not exceeding 190° into 1 : 4 : 5 : 8-*tetrahydroxy*-2 : 3 : 6 : 7-*diphthaloylthianthren*, dark green needles with a metallic lustre which do not melt below 360°; the dithiin is more advantageously prepared by the action of sodium sulphide on an aqueous suspension of 2 : 3-dibromo-1 : 4 : 9 : 10-anthra-

diquinone (cf. Dimroth, Friedmann, and Kämmerer, A., 1920, i, 444) in the absence of air. When heated with nitric acid (*d* 1·52) on the steam-bath it loses almost exactly a molecular proportion of sulphur and is doubtless transformed into diquinizarinthiophen, which, however, has not been more closely investigated. The dithiin yields a *monosodium* salt, $C_{28}H_{11}O_8S_2Na$, a *di-sodium* salt, and a *di-potassium* salt; greater proportions of base could not be introduced into the molecule. It is converted by alkaline hyposulphite solution or by zinc dust and alkali hydroxide into a blood-red vat from which *octahydroxydianthracenedithiin* separates in brown flocks after addition of acid; it has m. p. 238—244°. The corresponding *octabenzoate* crystallises in pale yellow needles, m. p. 240—244°. Tetrahydroxydiphthaloylthianthren is converted by benzoyl chloride in the presence of boiling nitrobenzene into the corresponding *tetrabenzoate*, a greenish-yellow, crystalline powder which does not melt below 360°, and by acetic anhydride in the presence of dehydrating agents into the *diacetate*, brown leaflets.

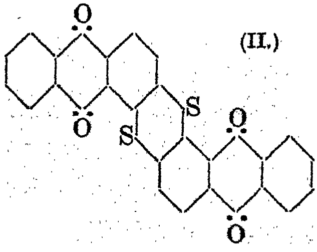
2 : 3-Dichloro-1 : 4-diaminoanthraquinone is converted by crystalline sodium sulphide at 210° into 1 : 4 : 5 : 8-*tetra-amino*-2 : 3 : 6 : 7-*diphthaloylthianthren*, $C_{28}H_{16}O_4N_4S_2$, small, dark blue needles which do not melt below 360°; with alkaline sodium hyposulphite solution it yields a red vat from which ammonia is evolved at 50—60°. Benzoylation of the vat leads to the production of the expected *octabenzoyl* derivative, $C_{84}H_{52}O_{12}S_2$, long, pale yellow, prismatic needles, m. p. 302° (decomp.). 1 : 4 : 5 : 8-*Tetrabenzoylamino*-2 : 3 : 6 : 7-*diphthaloylthianthren* crystallises in small, greenish-yellow, lustrous needles, which do not melt below 360°.

The presence of two benzoylamino groups in the vicinal position to the halogen atoms of 2 : 3-dichloro-1 : 4-dibenzoylaminoanthraquinone appears to inhibit the formation of the dithiin ring, since the substance is converted by sodium sulphide at 180° into the phenanthridone (I), microscopic, green needles which do not melt below 300°.

(I.)

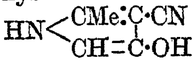


(II.)



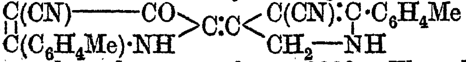
3 : 4 : 7 : 8-*Diphthaloylthianthren* [*thioindanthren*] (II), dark green, coppery needles, which do not melt below 360°, is prepared from 1 : 2-dibromoanthraquinone and sodium sulphide at 190°. With alkaline sodium hyposulphite solution, it gives a blood-red vat from which the expected *tetrabenzoate*, yellow needles, is obtained by the action of benzoyl chloride. H. W.

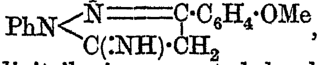
Hydroxypyrrole Derivatives [IV] and certain Reactions of Chloroacetyldiacetonitriles. E. BENARY and G. SCHWOCH (*Ber.*, 1924, **57**, [*B*], 332—339; cf. Benary and Lau, A., 1923, i, 366).—The remarkable formation of dyes when treated with alcoholic or liquid ammonia appears to be a general property of halogenoacyl derivatives of dinitriles containing an aromatic substituent and an unsubstituted imino group; when the latter contains a substituent, the normal formation of hydroxypyrroles is observed.

Chloroacetyldiacetonitrile, $NH_2{\cdot}CMe{:}C(CN){\cdot}CO{\cdot}CH_2Cl$, is converted by methyl-alcoholic ammonia into 4-*hydroxy*-2-*methylpyrrole*-3-*nitrile*,  $HN<\begin{matrix}CMe{:}C{\cdot}CN\\ CH{=}C{\cdot}OH\end{matrix}$, which is too unstable to permit its isolation in the homogeneous condition; it is characterised by its conversion into 5-*benzeneazo*-4-*keto*-2-*methylpyrroline*-3-*nitrile*, orange needles, decomp. 240°, by benzenediazonium solution, and by formaldehyde into *methylenebis*-4-*keto*-2-*methylpyrroline*-3-*nitrile*, an orange precipitate, decomp. about 250°.

C-*Chloroacetyl*-p-*toluacetodinitrile*,

$NH_2{\cdot}C(C_6H_4Me){:}C(CN){\cdot}CO{\cdot}CH_2Cl$,

matted needles, m. p. 166—168°, is prepared from *p*-toluacetodinitrile and chloroacetyl chloride in the presence of pyridine; it is converted by methyl-alcoholic ammonia into the *dye*,  $\begin{matrix}C(CN)\text{——}CO\\ C(C_6H_4Me){\cdot}NH\end{matrix}>C{:}C<\begin{matrix}C(CN){:}C{\cdot}C_6H_4Me\\ CH_2\text{—}NH\end{matrix}$, H_2O, a dark, violet-red powder, decomp. about 200°. The chloro compound is transformed by potassium hydrogen sulphide in alcoholic solution into the corresponding *sulphide*, $[NH_2{\cdot}C(C_6H_4Me){:}C(CN){\cdot}CO{\cdot}CH_2]_2S$, colourless prisms, decomp. 218·5—220°.

p-*Methoxybenzoacetodinitrile*, coarse, colourless prisms, m. p. 118°, is prepared by the action of sodium wire on anisonitrile and acetonitrile dissolved in hot benzene. It is converted by treatment in warm alcoholic solution with dilute hydrochloric acid into p-*methoxyphenyl cyanomethyl ketone*, $C_6H_4(OMe){\cdot}CO{\cdot}CH_2{\cdot}CN$, prisms, m. p. 130·5°; this ketone, with phenylhydrazine and glacial acetic acid in cold alcoholic solution, affords the *phenylhydrazone*, soft needles, m. p. 135—136°, which when heated above its m. p. or boiled with dilute acetic acid passes into 5-*imino*-1-*phenyl*-3-p-*methoxyphenylpyrazolone*,  $PhN<\begin{matrix}N\text{===}C{\cdot}C_6H_4{\cdot}OMe\\ C({:}NH){\cdot}CH_2\end{matrix}$, lustrous leaflets, m. p. 188°. The dinitrile is converted by hydroxylamine hydrochloride in boiling, aqueous-alcoholic solution into 5-*imino*-3-p-*methoxyphenyl*iso*oxazolone*, prisms, m. p. 136—137°. C-*Chloroacetyl*-p-*anisylacetodinitrile*, $C_{12}H_{11}O_2N_2Cl$, needles, m. p. 164°, is converted by methyl-alcoholic ammonia into the dark, violet-red *dye*, $C_{24}H_{18}O_3N_4$ (cf. formula above), decomp. 200° after darkening at 185°, and by potassium hydrogen sulphide into the *sulphide*, $[OMe{\cdot}C_6H_4{\cdot}C(NH_2){:}C(CN){\cdot}CO{\cdot}CH_2]_2S$, a crystalline powder, m. p. 196—197° (decomp.) after darkening and softening at 190°.

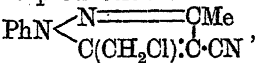
C-*Chloroacetyl*-N-p-*anisyldiacetonitrile*, $C_{13}H_{13}O_2N_2Cl$, lustrous needles, m. p. 80—81·5°, is converted by alcoholic potassium hydroxide solution into 3-*hydroxy*-1-p-*anisyl*-5-*methylpyrrole*-4-*nitrile*, matted needles, m. p. 190—192° (decomp.).

N-*Phenyl*-α-*anilinoacetylbenzoacetodinitrile*, prepared from chloroacetylbenzoacetodinitrile and aniline, decomposes at 258—260° when rapidly heated; with mercuric chloride and dilute hydrochloric acid it yields the additive *compound*, $C_{23}H_{19}ON_3,HCl,HgCl_2$, pale yellow needles, m. p. 172°. When boiled with an excess of glacial acetic acid the base yields α-*acetanilidoacetyl*-β-*anilino*-β-*phenylacrylamide*, $NHPh{\cdot}CPh{:}C(CO{\cdot}CH_2{\cdot}NAcPh){\cdot}CO{\cdot}NH_2$, colourless prisms, decomp. 296—298°, which is also obtained from chloroacetylbenzoacetodinitrile, aniline, and glacial acetic acid at 115—120°.

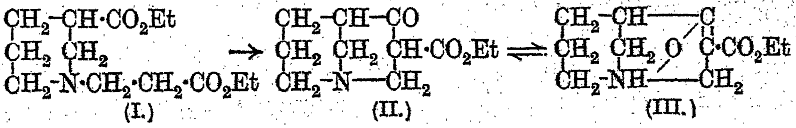
C-*Anilinoacetyl*-N-*phenyldiacetonitrile*,

$$NHPh{\cdot}CMe{:}C(CN){\cdot}CO{\cdot}CH_2{\cdot}NHPh,$$

small needles, m. p. 214—216° when rapidly heated, is obtained from chloroacetyldiacetonitrile and aniline or from the latter and *C*-chloroacetyl-*N*-phenylbenzoacetodinitrile; it gives a lemon-yellow *picrate*, m. p. 165—166° after previous softening, and the additive *compound*, $C_{18}H_{17}ON_3,HCl,HgCl_2$, colourless needles, decomp. 230° after darkening at 215°.

The action of phenylhydrazine on chloroacetyldiacetonitrile leads somewhat unexpectedly to the production of 5-*chloromethyl*-1-*phenyl*-3-*methylpyrazole*-4-*nitrile*,  $\mathrm{PhN}<\begin{matrix}\mathrm{N{=\!=\!=}CMe}\\ \mathrm{C(CH_2Cl){:}C{\cdot}CN}\end{matrix}$, needles, m. p. 130·5° after softening, which is also obtained from cyanoacetone phenylhydrazone and chloroacetyl chloride. It is hydrolysed to 5-hydroxymethyl-1-phenyl-3-methylpyrazole-4-carboxylic acid (cf. Benary, A., 1910, i, 434). Treatment with alcoholic potassium hydroxide solution transforms it into 5-*ethoxymethyl*-1-*phenyl*-3-*methylpyrazole*-4-*nitrile*, slender needles, m. p. 68·5°, which is unaffected by boiling, concentrated hydrochloric acid. The chloride is converted by methyl-alcoholic ammonia at 50—60° into 5-*aminomethyl*-1-*phenyl*-3-*methylpyrazole*-4-*nitrile*, long, colourless needles, m. p. 58—59° (*picrate*, pale yellow leaflets, m. p. about 250—251° [decomp.]) from which 5-*hydroxymethyl*-1-*phenyl*-3-*methylpyrazole*-4-*nitrile*, needles, m. p. 114—116°, is obtained by means of nitrous acid. H. W.

Synthesis of a New Bicyclic Nitrogen Ring. *iso*Granatanine Derivatives. Preparation of an Isomeride of Homococaine. S. M. McElvain and R. Adams (*J. Amer. Chem. Soc.*, 1923, **45**, 2738—2750).—Ethyl nipecotinate (piperidine-3-carboxylate) on condensation with ethyl β-chloropropionate in alcoholic solution in the presence of silver oxide yields ethyl (3-carbethoxypiperidino)-propionate (I), this being converted by sodium in xylene solution into ethyl *iso*granatonine carboxylate (II).



(I.) (II.) (III.)

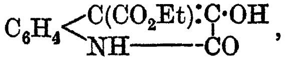
Reduction of the ketone converts it into ethyl granatolinecarboxylate, and benzoylation of the latter yields a compound isomeric with homococaine. It is a less efficient local anæsthetic than cocaine, and is considerably more toxic than the latter.

Nicotinic acid nitrate was obtained by adding nicotine to nitric acid (*d* 1·42) and heating at 100° for several hours. The nitrate was converted into the hydrochloride by heating with hydrochloric acid, removing excess of the latter in a vacuum, dissolving the product in water, and precipitating with alcohol. Pure nicotinic acid was then obtained in the usual manner. Ethyl nicotinate was obtained by treating nicotinic acid (or its hydrochloride) successively with thionyl chloride and alcohol (excess of chloride being removed intermediately). Nipecotinic acid was prepared by the reduction of nicotinic acid hydrochloride with hydrogen in the presence of platinum oxide catalyst (cf. Freudenberg, A., 1919, i, 93). *Ethyl nipecotinate* is a colourless, water-soluble liquid, b. p. 102—104°/7 mm., d_{20}^{20} 1·0121, n_D^{19} 1·4592 (*hydrochloride*, needles, m. p. 110—111°); it may also be obtained (less satisfactorily) by the catalytic reduction of ethyl nicotinate hydrochloride in alcoholic solution, and by the reduction of ethyl nicotinate in alcoholic acetic acid. *Ethyl* (3-*carbethoxypiperidino*)*acetate*, obtained from ethyl nipecotinate and ethyl chloroacetate in presence of finely powdered silver oxide, has b. p. 147—149°/5 mm., d_{20}^{20} 1·0684, n_D^{18} 1·4607. The free *acid*, obtained by hydrolysis of the ester or by condensing nipecotinic acid with chloroacetic acid in the presence of hydrochloric acid, forms white crystals, m. p. 268—270° (decomp.). *Ethyl* (3-*carbethoxypiperidino*)*propionate*, obtained similarly from ethyl nipecotinate and ethyl-β-chloropropionate or from nipecotinic acid and β-chloropropionic acid, has b. p. 159—161°/5 mm., d_{20}^{20} 1·0452, n_D^{18} 1·4605. *Ethyl* iso*granatoninecarboxylate hydrochloride* forms white, microscopic crystals, m. p. 187—189°; it is extremely soluble in water and gives a deep reddish-purple coloration with ferric chloride. The keto-ester hydrochloride can be obtained crystalline by adding dry ether to its alcoholic solution until a faint cloudiness appears and then cooling to about −12°. *Ethyl* iso*granatoninecarboxylate* is a thick, colourless oil, b. p. 137—139°/8 mm., d_{20}^{20} 1·1381, n_D^{18} 1·5070; it gives a pronounced colour with acidified ferric chloride solutions. *Ethyl* iso*granatolinecarboxylate hydrochloride*, obtained by the reduction of the ketone with sodium amalgam in acid solution or by catalytic reduction in alcoholic solution in the presence of the platinum oxide catalyst, melts at 199—201°. An *isomeride* appears to be present in the mother-liquors left after crystallisation. The *benzoyl* derivative of the alcohol is obtained in the form of its hydrochloride as a white, crystalline powder.

An ethereal solution of the crude keto-ester (II) gradually deposits crystals which from their solubility in organic solvents probably consist of compound (III). F. G. P.

Pepper-substances. III. The Chavicine of Black Pepper. II. E. Ott and O. Lüdemann (*Ber.*, 1924, **57**, [*B*], 214—216).—Chavicine is purified by dissolution in benzene, addition of stannic bromide, and precipitation of the additive compound (as a resinous mass) by means of ether. Analysis of the chavicine, regenerated after further dissolution in benzene and precipitation with ether, confirms the previous conclusion (Ott and Eichler, A., 1922, i, 1026) that it is stereoisomeric with piperine. Treatment of purified chavicine with alcoholic alkali hydroxide solutions yields unchanged material, *iso*chavicic acid, and piperidine; wax alcohols and fatty acids are not produced as is the case when crude chavicine is employed. H. W.

Ester Condensations with Ethyl *o*-Aminophenylacetate and Oxindole. W. Wislicenus and H. Bubeck (*Annalen*, 1924, **436**, 113—124).—It was expected that by condensing ethyl *o*-aminophenylacetate (Neber, A., 1922, i, 545) with ethyl formate, indole-3-carboxylic acid would be formed, but actually the product was oxindole-3-aldehyde (Friedländer, A., 1910, i, 592). Ethyl oxalate with the amino ester gave ethyl 2 : 3-dihydroxycinchoninate,



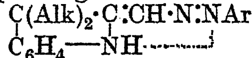
$$C_6H_4<\begin{matrix}C(CO_2Et){:}C{\cdot}OH\\ NH\text{———}CO\end{matrix},$$

together with a little oxindole-3-glyoxylic ester. Oxindole-3-aldehyde, obtained as above or from oxindole itself, forms yellow needles, m. p. 205—206°, and its anil has m. p. 254°. *Oxindole-3-glyoxylic acid,* the ester of which was obtained by condensing oxindole and ethyl oxalate, forms orange-yellow leaflets, m. p. 262—265° (decomp.); *anilide*, yellow leaflets, m. p. 261° (decomp.). The *ethyl* ester crystallises in orange needles, m. p. 187—188°, gives a green, crystalline *copper* salt, a *benzoyl* derivative (yellow needles, m. p. 160—161°), an *anil* (yellow prisms, m. p. 191—193°), and the corresponding *compound* with α-naphthylamine (m. p. 190°). Titration with bromine indicates that ethyl oxindole-3-glyoxylate exists solely in the *enolic* form. When treated with phenylhydrazine, it gives a mixture of the *phenylhydrazide* of the acid (needles, m. p. 238—239°) and the *phenylhydrazone* of the ester (yellow prisms, m. p. 160—164°), but at higher temperatures a *substance,* $C_{16}H_{11}O_2N_3$, crystallising in colourless needles, which decomposes at 265°. The *phenylmethylhydrazone* of the ethyl ester forms yellowish-brown prisms, m. p. 139°. *Methyl oxindole-3-glyoxylate* forms yellow needles, m. p. 167—169° (decomp.), and gives a *phenylhydrazone,* m. p. 197° (decomp.), which again gives the above compound, $C_{16}H_{11}O_2N_3$, when boiled with glacial acetic acid.

Ethyl 2 : 3-*dihydroxycinchoninate* forms needles, sintering about 210°, melting at 227—228°, and decomposing at 230°. It is a weak acid, giving crystalline ammonium and hydrazine salts. The *acid* forms white needles and decomposes without melting at 180°, giving 2 : 3-dihydroxyquinoline (Madelung, A., 1913, i, 92). Its *anilide* forms needles, m. p. 260° (decomp.). The *benzoyl* and *acetyl* derivatives of the ester (only the 3-hydroxy group reacted in each case) melt at 182—183° and 190°, respectively. W. A. S.

[Tri-indolylmethanes and Aldehydes, Ketones, Ketonic Esters, and Keto-nitriles of Substituted Indoles.] H. FISCHER (*Ber.*, 1924, 57, [*B*], 356).—2-Methylindole-3-aldehyde (cf. Fischer and Pisbor, this vol., i, 86) has been obtained previously by Barger (A., 1917, i, 476). H. W.

Mechanism of Diazo Coupling Reactions. IV. Azo Dyes from 2-Methylenetrialkylindolines. W. KÖNIG and J. MÜLLER (*Ber.*, 1924, 57, [*B*], 144—149; cf. A., 1923, i, 862).—2-Methylene-1 : 3 : 3-trialkylindolines couple with diazonium salts to yield azo dyes whereby the alkyl group in position 1 is removed as the corresponding alcohol. The new compounds are of the general type,



$\begin{array}{l} C(Alk)_2{\cdot}C{:}CH{\cdot}N{:}NAr \\ C_6H_4\text{—}NH \end{array}$

, which becomes somewhat modified when a chromophoric group is present in the para-position in the diazonium component. The facility with which coupling occurs depends on the nature of the 3-alkyl groups.

The following compounds are described: 1 : 2 : 3 : 3-*Tetramethylindoleninium bromide*, pale yellow crystals, m. p. 252° (decomp.), and the corresponding *perchlorate*, long, colourless needles, m. p. 192° (decomp.). 2-Methyl-1 : 3 : 3-triethylindoleninium *picrate*, yellow needles, m. p. 180°, and the very hygroscopic *chloride*, slender, colourless needles, m. p. 131°. 1 : 2-*Dimethyl*-3 : 3-*diethylindoleninium picrate*, dark yellow needles, m. p. 167° (the corresponding *chloride* and *perchlorate* are extremely hygroscopic). 2 : 3 : 3-*Trimethyl*-1-*ethylindoleninium perchlorate*, needles, m. p. 197° (decomp.).

2-Benzeneazomethylene-3 : 3-dimethylindoline is isolated as the *hydrochloride*, $C_{17}H_{18}N_3Cl$, m. p. 186° (decomp.), by treatment of a solution of 1 : 2 : 3 : 3-tetramethylindolinium iodide (or bromide) with sodium hydroxide and addition of benzenediazonium chloride to the emulsion of the methylene base. 2-p-*Nitrobenzeneazomethylene*-3 : 3-*dimethylindoline*, prepared in a similar manner from 2-methylene-1 : 3 : 3-trimethylindoline or 2-methylene-1-ethyl-3 : 3-dimethylindoline, crystallises in reddish-brown leaflets, m. p. 168°; the corresponding *hydrochloride*, brownish-red needles, decomp. about 286°, the *hydrobromide*, brownish-red needles, decomp. 250°, and the *acetate*, leaflets, are described. 2 : 4′-*Nitro*-2′-*methoxybenzeneazomethylene*-3 : 3-*dimethylindoline* forms lustrous, steel-blue needles, m. p. 211° (*hydrochloride* [$+CH_3{\cdot}CO_2H$], m. p. 128°, and subsequently decomp. about 290°). 2-*p*-Nitrobenzeneazomethylene-3 : 3-diethylindoline could not be caused to crystallise; the *hydrochloride*, brownish-yellow needles, has m. p. 280° (decomp.). 2-p-*Acetylbenzeneazomethylene*-3 : 3-*dimethylindoline* crystallises in lustrous, red needles, m. p. 191°; the *hydrobromide* forms reddish-brown needles, m. p. 264°. H. W.

Supposed Syntheses from Ethyl Isatin-1-carboxylate. A. HANTZSCH (*Ber.*, 1924, 57, [*B*], 195—199).—A criticism of the work of Heller (A., 1918, i, 309). Heller's 2 : 3-dihydroxy-2 : 3-dihydroindole-2-carboxylic acid is shown to be formylisatoic acid, $CHO{\cdot}NH{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$, since its production from ethyl isatin-

1-carboxylate by the action of warm water or cold sulphuric acid (50%) is accompanied by that of acetaldehyde whilst, also, it is hydrolysed in alkaline solution to isatoic and formic acids; this conclusion is confirmed by the analysis of the ethyl ester, m. p. 67°. The supposed "lactone-like anhydride," m. p. 108°, is proved to be 1-formylisatin, since its optical properties are almost identical with those of 1-acetylisatin; attempts to prepare it directly from isatin and formic acid in the presence of dehydrating agents were, however, unsuccessful. Heller's 2 : 4-dihydroxy-1 : 2 : 3 : 4-tetrahydroquinoline-2-carboxylic acid is, in reality, formylanthranilic acid, which is transformed by acetic anhydride and sodium acetate into acetylanthranilic acid (Heller's hydroxydihydroquinoline-2-carboxylic acid, m. p. 184°). The observed formation of yellow solutions of the colourless formylisatoic acid in water and anhydrous solvents is due to the ready production of 1-formylisatin. H. W.

Catalytic Hydrogenation of Pyridine. N. Zelinsky and P. Borisoff (*Ber.*, 1924, **57**, [*B*], 150—153).—Pyridine is very readily hydrogenated to piperidine in the presence of platinised asbestos (40%) at 150°. The catalyst does not become poisoned, since it retains its ability to cause the hydrogenation of benzene. At about 250°, it smoothly effects the dehydrogenation of piperidine, but, after use, it is no longer capable of bringing about the reduction of benzene or pyridine or the dehydrogenation of *cyclo*hexane. Palladised asbestos is a still more effective agent for the hydrogenation of pyridine at 150°; after use, however, it is found to have lost all activity towards benzene. It readily causes the dehydrogenation of piperidine, but not of *cyclo*hexane at 250°; after use, it is incapable of effecting hydrogenation.

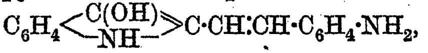
The preparation of the highly active catalyst is effected in the following manner. Asbestos, which has been washed with acid and ignited, is soaked in a concentrated, faintly acid solution of platinum or palladium chloride at the temperature of boiling water and subsequently immersed in cold formaldehyde solution (35—40%). It is then treated with concentrated sodium hydroxide solution (40—50%), initially at 0° and finally on the water-bath. The product is washed thoroughly with water, immersed in dilute acetic acid solution, and again washed until the filtrate is neutral in reaction. It is dried for a short period at 110°. H. W.

Complex [Pyridine, Pyrazine, and Quinoxaline] Salts of Bivalent Iron. H. Ley, C. Schwarte, and O. Münnich.—(See ii, 228.)

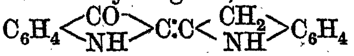
The Product of the Action of Acidic Reducing Agents on Indigotin. W. Madelung and P. Siegert (*Ber.*, 1924, **57**, [*B*], 222—233).—The reduction of indigotin in the presence of acids leads to the opening of the ring with formation of 2 : 2′-diamino-ω-styrylacetophenone.

The gradual addition of indigotin and finely-divided iron to an almost saturated solution of hydrogen chloride in alcohol leads to the separation of *2 : 2′-diamino-ω-styrylacetophenone hydrochloride*, $NH_2 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CH\colon CH \cdot C_6H_4 \cdot NH_2,HCl$, pale brown crystals; the corresponding *picrate, sulphate,* and perchlorate are described. The hydrochloride is converted by acetic anhydride in the presence of pyridine into the *acetyl* derivative, $C_{20}H_{20}O_3N_2$, colourless leaflets, m. p. 181° (the *perchlorate* is described). With formaldehyde and benzaldehyde, respectively, the base gives the *compounds,* $C_{17}H_{16}ON_2$, greenish-yellow crystals, and $C_{23}H_{20}ON_2$, slender, greenish-yellow crystals. The conversion of indigotin into 2 : 2′-diamino-ω-styrylacetophenone can be effected by ferrous chloride or by the addition of indigo-white to alcoholic hydrogen chloride, whereby disproportionation occurs accompanied by precipitation of indigotin.

2 : 2′-Diamino-ω-styrylacetophenone is very easily dehydrogenated. The hydrochloride is converted by solution in warm pyridine and exposure to air into 2-o-*aminostyrylindoxyl,*

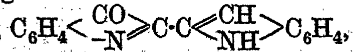


$C_6H_4<\begin{matrix}C(OH)\\NH\end{matrix}>C\cdot CH{:}CH\cdot C_6H_4\cdot NH_2$, small needles, m. p. 161°, which is readily oxidised further; it gives a *monoacetyl* derivative, decomp. above 250°. Deoxyindigotin,



$$C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C{:}C<\begin{matrix}CH_2\\NH\end{matrix}>C_6H_4$$

(cf. Borsche and Meyer, A., 1922, i, 55), is also obtained by the action of air on solutions of 2 : 2′-diamino-ω-styrylacetophenone in pyridine and is the sole product of the action of alcoholic solutions of potassium hydroxide or sodium alkoxide on the base. The ultimate product of the dehydrogenation of 2 : 2′-diamino-ω-styrylacetophenone is the *substance,*



$C_6H_4<\begin{matrix}CO\\-N\end{matrix}\geqslant C\cdot C\leqslant\begin{matrix}CH\\NH\end{matrix}>C_6H_4$, cocoa-brown, rhombic leaflets (*monoacetyl* derivative, pale yellow leaflets, decomp. 245—250°). When its solution in pyridine is exposed to air for 3—4 days the dimeric *compound,* $(C_{16}H_{10}ON_2)_2$, separates in the form of dark violet-blue, slender needles. A second dimeric *compound,* $(C_{16}H_{10}ON_2)_2$, is obtained by the action of concentrated acids on a solution of the monomeric substance, $C_{16}H_{10}ON_2$; the latter, which forms orange crystals, is immediately coloured green, probably owing to the formation of an unstable salt, and subsequently rapidly passes into the tile-red salt of the dimeride, which can also be obtained by dehydrogenation or disproportionation from the compounds $C_{16}H_{16}ON_2$, $C_{16}H_{14}ON_2$, and $C_{16}H_{12}ON_2$. It has well-marked basic properties and gives sparingly soluble salts with mineral acids, the most characteristic of which is the *hydriodide,* $C_{32}H_{20}O_2N_4,HI$. The *diacetyl* derivative, $C_{36}H_{24}O_4N_4$, is a red, crystalline powder. When boiled with an alcoholic solution of formaldehyde, the base is converted into the *substance,* $C_{33}H_{22}O_2N$ (orange-yellow crystals), whereas it is transformed by a boiling solution of sodium methoxide in methyl alcohol into the *compound* $C_{32}H_{25}O_2N_4$, canary-yellow, rhombic leaflets. H. W.

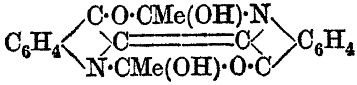
Imines, Anils, and Hydrazones of Indigotin and the Stereochemical Configuration of the Indigoids. W. Madelung and O. Wilhelmi (*Ber.*, 1924, 57, [*B*], 234—241).—The carbonyl and imino groups of indigotin are so indifferent towards the usual reagents that their presence cannot be established in the customary manner. On the other hand, derivatives such as the oximes, phenylhydrazones, and azines can easily be prepared when di-iminoindigotin (Madelung, A., 1913, i, 904) is used as initial material; of these, indigotindioxime has already been described (Madelung, A., 1914, i, 738). The stability of indigotin suggests that there is an intimate connexion between the carbonyl and imino groups such as has been indicated by the constitutions proposed by Claasz (A., 1916, i, 840) and by Lifschitz and Lourié (A., 1917, i, 586). These formulæ do not, however, appear to be satisfactory, since they are valid only for indigotin itself, and cannot be extended to the derivatives of it which are now described; these are very closely related (optically) to indigotin. It is suggested that the oxygen atom of the carbonyl group is joined by a subsidiary valency either to the hydrogen atom of the imino group in the opposite half of the molecule, thus yielding a new six-membered ring, as has been proposed by Scholl (Georgievics, "Die Biziehungen zwischen Farbe u. Konstitution von Farbstoffen," 1920), or to the imino nitrogen atom, thus giving a new five-membered ring.

Indigotinbisphenylhydrazone, $C_{16}H_{10}N_2(:N\cdot NHPh)_2$, red needles, m. p. 219—220° (decomp.), is prepared by the gradual addition of phenylhydrazine to a solution of di-iminoindigotin acetate in glacial acetic acid and subsequent treatment of the hot saturated solution of the product in alcohol with anhydrous potassium carbonate; it separates from acetic acid in green crystals ($+2CH_3\cdot CO_2H$), m. p. 202—204°. The *hydrochloride*, $C_{28}H_{22}N_6,HCl$, green needles, and the *picrate*, $C_{28}H_{22}N_6,2C_6H_3O_7N_3$, green needles, are described. In a similar manner, di-iminoindigotin acetate is converted by hydrazine hydrate into *indigotinazine acetate*, $C_{16}H_{10}O_4,C_2H_4O_2$, long, somewhat unstable needles, m. p. above 300° after previous change; the free base is too unstable to isolate. *Indigotindianilide acetate*, $C_{28}H_{20}N_4,C_2H_4O_2$, dark, bluish-green crystals, is obtained from di-iminoindigotin acetate, aniline, and glacial acetic acid in boiling alcoholic solution; when dissolved in xylene and treated with anhydrous sodium carbonate, it gives the corresponding free base (cf. Grandmougin and Dessoulavy, A., 1910, i, 73). *Dimethyliminoindigotin acetate*, prepared from di-iminoindigotin acetate and methylamine in boiling alcoholic solution, has m. p. 252—254°; the corresponding *base* crystallises in blue needles. The action of acetic anhydride on the imino acetate affords *diacetyliminoindigotin*, aggregates of dark blue needles, m. p. 202°.

Indoleazobenzene, $C_{11}H_{11}N_3$, yellowish-brown crystals, m. p. 133—134°, is prepared by the gradual addition of a methyl-alcoholic solution of indole to an alkaline solution of diazotised aniline. H. W.

Alkyl and Acyl Derivatives of Leuco-indigotin and Indoxyl.

W. MADELUNG (*Ber.*, 1924, **57**, [*B*], 241—252).—A study of the action of benzyl chloride on alkaline solutions of leuco-indigotin leads the author to the conclusion that, contrary to previous views, alkylation leads primarily to the production of *C*-substituted derivatives which readily undergo fission to substituted indoxyls. The formation of two diacetyl-leuco-indigotins is very difficult to interpret; it is suggested that the acetyl groups are not present as such but form a bridge between the hydroxy and imino groups as indicated in the annexed formula. The stereoisomerism is due to the presence of two asymmetric carbon atoms in the two new rings (cf. Madelung and Hagen, A., 1916, i, 840).



$$C_6H_4\genfrac{<}{}{0pt}{}{C\cdot O\cdot CMe(OH)\cdot N}{N\cdot CMe(OH)\cdot O\cdot C}\!>\!C{=}C\!<\!C_6H_4$$

[With O. Haller.]—Indigo white is converted by methyl sulphate in the presence of sodium hydroxide into a dimethyl derivative, rhombic leaflets, m. p. above 235° (decomp.) after darkening at 200° (cf. Grandmougin, A., 1922, i, 470); it gives a *picrate*, dark violet needles, m. p. 173°, and is converted by nitrous acid in the presence of glacial acetic acid into indigotin.

Monobenzyl-leuco-indigotin, $C_{23}H_{18}O_2N_2$, ochre-yellow needles, m. p. 183°, is prepared by the action of benzyl chloride on leuco-indigotin at the ordinary temperature. When an excess of benzyl chloride is used under similar conditions, two isomeric *dibenzyl-leuco-indigotins* are formed. The main product, pale greenish-yellow crystals, m. p. 203°, resembles the dimethyl compound in yielding fluorescent solutions; it is unstable in hot solutions in the presence of acids. It is regarded as the *C*-dibenzyl compound, $C_6H_4<\genfrac{}{}{0pt}{}{CO-}{NH}>C(CH_2Ph)\cdot C(CH_2Ph)<\genfrac{}{}{0pt}{}{CO-}{NH}>C_6H_4$. The second substance, colourless needles, m. p. 192°, is stable in organic media, but more sensitive towards permanganate than its isomeride; it is considered to be the dibenzyl ether of leuco-indigotin. The substance, m. p. 203°, is converted by boiling glacial acetic acid into benzylideneindoxyl, $C_{15}H_{11}ON$.

When treated in alkaline solution with an excess of benzyl chloride at 70—80°, leuco-indigotin suffers fission and the primary products become further benzylated, whereby 2 : 2′-dibenzylindoxyl, yellow crystals, m. p. 174—175° (*nitroso* derivative, pale yellow, lustrous leaflets, m. p. 135°), and 2-*benzylindoxyl benzyl ether*, colourless, slender needles, m. p. 198—199°, are formed; the latter substance is readily oxidised by permanganate, but is stable towards nitrous acid.

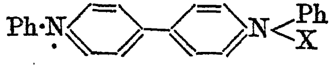
1-Acetylindoxyl gives a *phenylhydrazone*, $C_{16}H_{15}ON_3$, pale yellow needles, m. p. 154°, and an *oxime hydrochloride*, $C_{10}H_{10}O_2N_2,HCl$, colourless needles, m. p. 139°.

Indigotin is converted when heated with acetic anhydride, zinc dust, and acetyl chloride into a *compound*, $C_{20}H_{14}O_3N_2$, yellow needles, m. p. 209—210°, which is regarded as *diacetylanhydroleuco-indigotin*; the success of the preparation depends greatly on the purity of the materials and appears to be governed largely by experimental conditions. H. W.

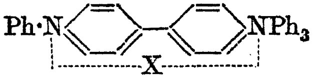
Spectroscopy of the Sulphonated Indigotins. W. C. Holmes (*J. Amer. Chem. Soc.*, 1924, **46**, 208—214).—The absorption spectra of the pure potassium salts of sulphonated indigotin in the visible spectrum have been measured under various conditions. The absorption maxima of the potassium salts in aqueous solution were :

monosulphonate, 608 $\mu\mu$; disulphonate, 610 $\mu\mu$; trisulphonate, 603 $\mu\mu$; tetrasulphonate, 590 $\mu\mu$. Data are supplied for their spectrophotometric identification and evaluation. F. A. M.

Free Ammonium Radicals. V. Comparison of 1 : 1′-Dibenzyl- and 1 : 1′-Diphenyl-4 : 4′-dipyridinium. E. Weitz, T. König, and L. von Wistinghausen (*Ber.*, 1924, **57**, [*B*], 153—175).—Further insight into the constitution of pyridinium radicals is obtained by a study of the reduction of 1 : 1′-diphenyl-4 : 4′-dipyridinium iodide, which has led to the isolation of deeply coloured compounds containing an atom of iodine united with a molecular proportion of the radical. The relationships are similar, but less obvious in the benzyl series (cf. Weitz and König, A., 1922, i, 1186). Compounds of this type are formulated by the authors as semiradicals (I), or intramolecular quinhydrones (II), whereas they



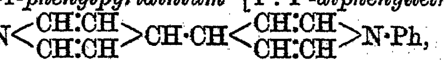
(I.)

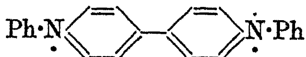


(II.)

have been regarded by Emmert (A., 1922, i, 1064) and Dimroth (A., 1923, i, 149) as quinhydrone-like products of the union of molecular proportions of the radical and the dihalogenide.

1 : 1′-Dibenzyl-4 : 4′-dipyridinium subiodide (cf. Emmert and Varenkamp, A., 1922, i, 1064) is obtained by the reduction of the di-iodide with metals or, more conveniently, by the action of the di-iodide on the radical; it crystallises in coarse platelets with a metallic reflex, m. p. about 190°, according to the rate of heating. It is reduced to the free radical by metallic sodium or an excess of dibenzyldipyridinium in alcoholic solution. The corresponding subchloride is isolated in blackish-violet, rhombohedral crystals, m. p. about 190° when rapidly heated; the molecular weight in boiling methyl alcohol is about half that required by the formula, $C_{24}H_{22}N_2Cl$.

1-Phenylpyridinium chloride, m. p. 105° (corresponding *perchlorate*, colourless needles, m. p. 221°), is conveniently prepared by boiling the so-called " pyridine dye " (from dinitrophenylpyridinium chloride or pyridine cyanobromide and aniline) with alcohol and concentrated hydrochloric acid and addition of ferric chloride solution; the additive salt, $C_{11}H_{10}NCl,FeCl_3$, is subsequently decomposed by the requisite amount of sodium carbonate. It is reduced by sodium amalgam in aqueous solution mainly to 1-*phenyl*-$\Delta^{1\cdot 4}$(?$\Delta^{1\cdot 2}$)-*dihydropyridine*, transparent crystals, m. p. 49—50° (the constitution of which is deduced from its properties, its molecular weight, and its conversion by iodine into 1-phenylpyridinium iodide); *bis*-1-*phenylpyridinium* [1 : 1′-*diphenyltetrahydro*-4 : 4′-*dipyridyl*],  $Ph\cdot N{<}{}^{CH:CH}_{CH:CH}{>}CH\cdot CH{<}{}^{CH:CH}_{CH:CH}{>}N\cdot Ph$, silvery leaflets, m. p. 136° (decomp.) after darkening at 100° when rapidly heated, is produced in minor amount. If, however, the reduction is effected in permanently neutral or faintly acid solution (for example, by sodium amalgam in the presence of aluminium sulphate), the leuco compound is alone formed; on the other hand, the dihydro product is almost exclusively produced if the solution is made alkaline from the commencement of the experiment. The action of iodine on 1 : 1′-diphenyltetrahydro-4 : 4′-dipyridyl proceeds in a complex manner, yielding 1 : 1′-diphenyl-4 : 4′-dipyridinium di-iodide, red prisms, m. p. about 360° (cf. König, A., 1923, i, 382); the corresponding perchlorate and picrate have m. p. 311° and 244°, respectively, whereas König (*loc. cit.*) gives m. p. 299° and 170°; 1-*phenylpyridinium iodide*, colourless, flattened prisms or anhydrous leaflets, m. p. 210° after darkening above 100°, is also produced, whilst about half the original material remains in the chloroform.

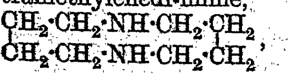
1 : 1′-*Diphenyl*-4 : 4′-*dipyridinium*,  is most conveniently prepared by dissolving 1 : 1′-diphenyltetrahydro-4 : 4′-dipyridyl in a warm mixture of pyridine and methyl alcohol and preserving the mixture in a closed, half-filled flask for about a week; it separates from the solution in red, rhombic crystals with a vivid blue reflex, decomp. above 180°. It decomposes readily when exposed to air. It is converted by iodine in all solvents with the exception of benzene, primarily into the subiodide (below) and finally into the red di-iodide. The radical may also be prepared by the reduction of an aqueous solution of the di-iodide with zinc dust. 1 : 1′-*Diphenyl*-4 : 4′-*dipyridinium subiodide*,

$$Ph\cdot C_5H_5\dot{N}\cdot C_5H_5NPhI,$$

is most conveniently prepared by mixing equivalent quantities of diphenyldipyridinium di-iodide and the corresponding leuco compound dissolved in acetone or chloroform; it crystallises in lustrous, steel-blue prisms, m. p. 318—319° (decomp.).

1 : 1′-Diphenyltetrahydro-4 : 4′-dipyridyl dissolved in chloroform is converted by a mixture of oxygen and carbon dioxide into 1 : 1′-*diphenyl*-4 : 4′-*dipyridinium hydrogen subcarbonate*, short prisms which appear violet by reflected, nearly black by transmitted light. The product is also obtained when a mixture of nitric oxide and carbon dioxide is used. H. W.

Cyclic Di-imines and their Decomposition. III. J. VON BRAUN, G. BLESSING, and F. ZOBEL (*Ber.*, 1924, **57**, [*B*], 185—191; cf. A., 1923, i, 840).—The catalytic hydrogenation of γ-phenoxy-*n*-butyronitrile in amyl-alcoholic solution (cf. A., 1923, i, 1088) gives a mixture of δ-phenoxybutylamine and di-δ-phenoxybutylamine; when subjected to slow distillation, the secondary base is transformed into phenol and *phenoxybutylpyrrolidine*, a colourless liquid, b. p. 170°/13 mm. (the hygroscopic *hydrochloride*, the *picrate*, yellow needles, m. p. 110°, and the *methiodide*, m. p. 123°, are described). It is converted by fuming hydrobromic acid at 100° into δ-*bromobutylpyrrolidine* (identified as the *chloroplatinate*, m. p. 133—134° after softening at about 130°), which is readily transformed into dipyrrolidinium bromide (cf. von Braun, A., 1916, i, 631). The salt is slowly converted by concentrated ammonia at 170—180° into ditetramethylenedi-imine,



$$\begin{array}{l}CH_2\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\\CH_2\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\end{array},$$

a colourless liquid, b. p. 95°/12 mm., d_4^{18} 0·902; the hygroscopic *hydrochloride*, the *chloroplatinate*, yellowish-red crystals, decomp. 207°, the *picrate*, m. p. 203—204°, the *benzenesulphonyl* compound, the *nitroso* derivative, the exceedingly hygroscopic *dimethiodide*, and the corresponding *chloride* and *chloroplatinate*, decomp. 257°, are described.

Tetramethylenepentamethylenedi-imine, a liquid, b. p. 110—112°/14 mm., d_4^{11} 0·920, is prepared similarly from the corresponding bromide; it yields a non-crystalline *benzenesulphonyl* derivative and *picrate*, a hygroscopic *hydrochloride*, a *chloroplatinate*, decomp. 190°, and a *di-methiodide*, $C_{13}H_{30}N_2I_2$, m. p. 247°, which is transformed through the *chloride* into the corresponding *chloroplatinate*, decomp. 248°.

Treatment of dipiperidinium bromide with aqueous ammonia (cf. A., 1907, i, 151) leads to the isolation of very small yields of *dipentamethylenedi-imine* (*dipiperidine*), b. p. 108—110°/12 mm., d_4^{17} 0·9195. The non-crystalline *picrate* and *nitroso* derivative, the hygroscopic *hydrochloride*, and the *chloroplatinate*, an orange-coloured, crystalline powder, decomp. 180°, are described. The *dimethiodide*, m. p. 272° (decomp.), and the corresponding *chloroplatinate*, decomp. 247°, have been prepared. H. W.

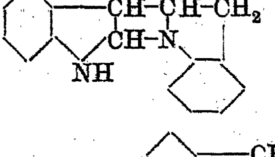
Discatole. B. ODDO and G. B. CRIPPA (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 31—34).—*Discatole*, $C_{18}H_{18}N_2$, obtained as hydrochloride by subjecting scatole, in anhydrous ethereal solution, to the action of a slow current of hydrogen chloride, forms white needles, m. p. 130°, and is free from the fæcal odour of scatole itself. Its *hydrochloride*, $C_{18}H_{18}N_2,HCl$, forms microscopic, highly refractive, prismatic crystals, m. p. 173°; its orange-red *picrate*,

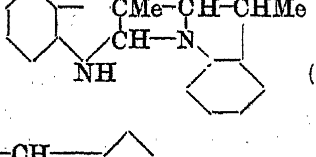
$$C_{18}H_{18}N_2,C_6H_3O_7N_3,$$

m. p. 170°, and its colourless *oxalate*, $(C_{18}H_{18}N_2)_2,C_2H_2O_4$, m. p. 180°, are described. It has not been found possible to obtain a triscatole.

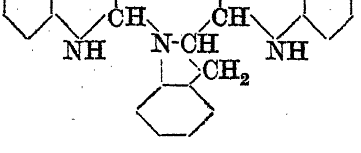
These results, in conjunction with the facts that indole gives both a dimeride and a trimeride, that 2-methylindole undergoes no such polymerisation, and that any of these polymerides yields only a mono-hydrochloride, indicate for di-indole, discatole, and tri-indole the formulæ (I), (II), and (III), respectively:

(I.)





(II.)



(III.)

T. H. P.

Dyes derived from Acenaphthenequinone. A. C. Sircar and S. K. Guha (*J. Chem. Soc.*, 1924, **125**, 335—340).—Azines produced by the condensation of acenaphthenequinone and of its 3 : 4-dinitro derivative with *o*-diamines, possess tinctorial properties not inferior to those of the corresponding derivatives of phenanthraquinone. Although insoluble in water, they can be used when freshly precipitated for dyeing wool. The azine sulphonic acids and azonium derivatives are also satisfactory dyestuffs. The reduction products of the 3 : 4-dinitroazines have probably the diaminodihydroazine structure (cf. T., 1922, **121**, 1950). Attempts to prepare 3-nitroacenaphthenequinone by the method of Rowe and Davies (T., 1920, **117**, 1349) always yielded a product containing the dinitro derivative. The following substances are described: *acenaphthatolazine*, $C_{12}H_6{<}^{N}_{N}{>}C_6H_3Me$, light brown needles, m. p. 232°. *Acenaphthanaphthazine*,

$$C_{12}H_6{<}^{N}_{N}{>}C_{10}H_6,$$

brownish-yellow needles, m. p. 290°. 3 : 4-*Dinitroacenaphthatolazine*, $(NO_2)_2C_{12}H_4{<}^{N}_{N}{>}C_6H_3Me$, orange-yellow needles, m. p. not below 290°. 3 : 4-*Dinitroacenaphthanaphthazine*,

$$(NO_2)_2C_{12}H_4{<}^{N}_{N}{>}C_{10}H_6,$$

scarlet-red, shining needles, m. p. not below 290°. 3 : 4-*Dinitroacenaphthaphenazine*, $(NO_2)_2C_{12}H_4{<}^{N}_{N}{>}C_6H_4$, orange-yellow plates, m. p. not below 290°. 3 : 4-*Dinitroacenaphthaphenazinazine*, $(NO_2)_2C_{12}H_4{<}^{N}_{N}{>}C_6H_2{<}^{N}_{N}{>}C_6H_4$, red, prismatic needles, no m. p. *Acenaphthanaphthazine-5′-sulphonic acid*, $C_{12}H_6{<}^{N}_{N}{>}C_{10}H_5{\cdot}SO_3H$, microscopic, brownish-yellow needles, m. p. not below 300°. 3 : 4-*Dinitroacenaphthanaphthazine-5′-sulphonic acid*, brown, amorphous precipitate. *Phenylacenaphthanaphthazonium chloride*,

$$C_{12}H_6{<}^{N\text{———}}_{NPhCl}{>}C_{10}H_6,$$

greenish-black powder, m. p. not below 290°. *Phenyl*-3 : 4-*dinitroacenaphthanaphthazonium chloride*, similar, m. p. 270°. *Naphthylacenaphthaphenazonium chloride*, dull, black powder, m. p. not below 290°. 3 : 4-*Diamino*-7 : 12-*dihydroacenaphthaphenazine*,

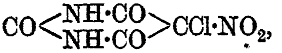
$$(NH_2)_2C_{12}H_4{<}^{NH}_{NH}{>}C_6H_4,$$

orange-red prisms, m. p. (with sublimation) above 290°. 3 : 4-*Diamino*-7 : 12-*dihydroacenaphthanaphthazine*, scarlet-red, rectangular plates. 3 : 4-*Dihydroxy*-7 : 12-*dihydroacenaphthaphenazine*, brick-red powder, subliming above 290°. F. G. W.

Action of Hydrazine on Uracil and Thymine. R. Fosse, A. Hieulle, and L. W. Bass (*Compt. rend.*, 1924, **178**, 811—813).—Uracil reacts with hydrazine to give carbamide and pyrazolone, the latter with xanthhydrol affording 1 : 2- or 1 : 4-*dixanthylpyrazolone*, colourless filaments, colouring at 195° and melting at 210—213° to a red liquid. Thymine, treated successively with hydrazine hydrate and xanthhydrol, affords dixanthylcarbamide and *dixanthyl*-4-*methylpyrazolone* (colourless crystals, m. p. about 202°), this substance also resulting by the action of xanthhydrol on the crude condensation product from hydrazine and ethyl formylpropionate. E. E. T.

Oxidation Products of Bilirubin. Detection of Urobilin. A. ADLER.—(See ii, 280.)

5-Nitrobarbituric Acids. H. BILTZ and K. SEDLATSCHECK (*Ber.*, 1924, **57**, [*B*], 339—349).—Violuric acid, decomp. 240—241° after darkening at 220° (cf. Biltz and Hamburger, A., 1916, i, 505) is converted by concentrated nitric acid into 5-nitrobarbituric acid, decomp. 180—181°, the yield being about 95% of that theoretically possible. The latter acid when suspended in ice-cold water and treated with chlorine yields 5-*chloro*-5-*nitrobarbituric acid*,



$CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CCl\cdot NO_2$, colourless, slender needles, decomp. 86—87°, which is decomposed by warm water into nitrobarbituric acid, carbamide, and chloropicrin and by bleaching powder solution into chloropicrin and carbamide. 5-*Bromo*-5-*nitrobarbituric acid*, long, slender needles, decomp. 108°, is decomposed by warm water in the same manner as the chloro compound. The position of the halogen atom in these acids is established by the observation that they are transformed by diazomethane into 5-halogeno-5-nitro-1 : 3-dimethylbarbituric acids (see later).

5-*Nitro*-1-*methylbarbituric acid*, $C_5H_5O_5N_3,2H_2O$, colourless, slender needles, decomp. 142—143°, is prepared in 92% yield from methylvioluric acid; the *ammonium, potassium, sodium* (+H_2O), and *barium* (+H_2O) salts are described. The acid is remarkably stable towards solutions of alkali hydroxides. 5-*Chloro*-5-*nitro*-1-*methylbarbituric acid*, colourless, hexagonal plates, decomp. 122—123°, is decomposed completely by boiling water into nitromethylbarbituric acid, methylcarbamide, chloropicrin, and carbon dioxide. 5-*Bromo*-5-*nitro*-1-*methylbarbituric acid* forms colourless, four-sided prisms, m. p. 137—138°.

5-Nitro-1 : 3-dimethylbarbituric acid, small, colourless needles, decomp. 148—149° (the sodium and *potassium* salts are described), is converted into 5-chloro-5-nitro-1 : 3-dimethylbarbituric acid, decomp. 150°, and 5-bromo-5-nitro-1 : 3-dimethylbarbituric acid, decomp. 152°.

5-*Nitro*-1-*ethylbarbituric acid*, $C_6H_7O_5N_3,H_2O$, forms colourless needles, decomp. 132—133°; the *ammonium, potassium, sodium, calcium*, and *strontium* salts are described. 5-*Chloro*-5-*nitro*-1-*ethylbarbituric acid* crystallises in colourless, rhombic leaflets, decomp. 127—128°. 5-*Bromo*-5-*nitro*-1-*ethylbarbituric acid* is a heavy, microcrystalline powder, decomp. 138—139°.

5-*Nitro*-1 : 3-*diethylbarbituric acid*, colourless octahedra, decomp. 116—117°, is prepared from diethylvioluric acid; it may also be obtained in poorer yield by the direct nitration of 1 : 3-diethylbarbituric acid, whereby diethylalloxan and tetraethylalloxantin are also produced; the *ammonium* salt, long, colourless needles, is described. 5-*Chloro*-5-*nitro*-1 : 3-*diethylbarbituric acid*, a heavy, crystalline precipitate, decomp. 53°, and 5-*bromo*-5-*nitro*-1 : 3-*diethylbarbituric acid*, a heavy, micro-crystalline powder, decomp. 63—64°, have been prepared.

Evidence is adduced against the existence of violantin and its alkyl derivatives. H. W.

Acetonylbarbituric Acid and some of its Derivatives. A. W. Dox and B. Houston (*J. Amer. Chem. Soc.*, 1924, **46**, 252—256).—The acetonyl group may be introduced directly at carbon atom 5 of barbituric acid by means of chloroacetone. Further substitution by halogen is readily effected, or by allyl, benzyl, and acetonyl. The less reactive alkyl halides, such as butyl bromide, do not react readily with acetonylbarbituric acid, but the acetonyl and alkyl groups may be introduced in the reverse order by treatment of the monoalkylbarbituric acid with chloroacetone. The acetonylalkylbarbituric acids are much less effective as hypnotics than the dialkylbarbituric acids with the same length of side chains.

It was not found possible to prepare ethyl acetonylmalonate from sodiomalonic ester and chloroacetone, but barbituric acid itself was alkylated readily in boiling aqueous solution.

Acetonylbarbituric acid forms flat, yellow crystals, m. p. 238—240° (decomp.); it liberates acetic acid from its salts. Halogenation yielded respectively *acetonylbromobarbituric acid*, white needles, decomp. about 143° without melting, and *acetonylchlorobarbituric acid*, white needles, which begin to decompose about 175° and melt about 245°. The following dialkylated acids were prepared by further treatment of acetonylbarbituric acid in the usual manner: *diacetonylbarbituric acid*, white needles, m. p. 264—266° (decomp.), *acetonylallylbarbituric acid*, large, white crystals, m. p. 216—217°, *acetonylbenzylbarbituric acid*, large, prismatic crystals, m. p. 224—225°; *acetonylethylbarbituric acid*, flat, white crystals, m. p. 238—239°. F. A. M.

Velocity of Spontaneous Oxidation of Uric Acid in Alkaline Solution. L. Piaux (*Compt. rend.*, 1924, **178**, 637—640; cf. Biltz and Robl, A., 1920, i, 883, and More, this vol., i, 315).—An aqueous solution containing 5 mols. of potassium hydroxide to 1 mol. of uric acid rapidly absorbs oxygen; with a smaller porportion of base oxidation is less rapid. A considerable quantity of ammonia is formed. On acidifying, carbon dioxide is evolved, and addition of alcohol then causes the precipitation of potassium oxonate, $C_4H_2O_4N_3K$. The main reaction may be written thus: $C_5H_4O_3N_4+O_2+H_2O=CO_2+NH_3+C_4H_3O_4N_3$.

Since allantoin was not formed in these oxidation processes, the author examined the action of air (1) on an alkaline solution of potassium allantoate, and (2) on an alkaline solution of uric acid which had previously (by means of permanganate) been oxidised to the extent of 1 atom of oxygen. (Solution 2, according to Biltz and others [*loc. cit.*] contains a substance which is oxidisable to an oxonate.) Neither (1) nor (2) absorbed oxygen.

E. E. T.

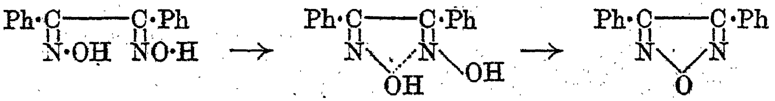
Action of Catalysts on the Oxidation of Uric Acid. Iron and Manganese (Hydroxides). L. PIAUX (*Compt. rend.*, 1924, **178**, 782—785; cf. preceding abstract).—The aërial oxidation of uric acid (1 mol.) in potassium hydroxide (5 mols.) solution, is accelerated by traces of ferric hydroxide, potassium oxonate being formed. Manganese oxide hydrates (obtained by using manganese lactate) accelerate the initial aërial oxidation but diminish the amount of oxonate formed, none of the latter being obtained when 1 mol. of lactate is originally taken per 5·6 mols. of uric acid. Allantoin takes its place, and is formed from the intermediate compound described by Biltz and Behrend (cf. A., 1921, i, 893).

E. E. T.

Ethylated Uric Acids. H. BILTZ and K. SEDLATSCHEK (*Ber.*, 1924, **57**, [*B*], 175—182).—The action of ethyl bromide on dipotassium urate in the presence of carbon tetrachloride at 110° leads to the production of moderate yields (12—13%) of 3 : 7 : 9-triethyluric acid, colourless aggregates of needles, m. p. 204°; the product is probably identical with the triethyluric acid obtained by Drygin in 1864 by the action of ethyl iodide on lead urate. The constitution of the acid is deduced from its oxidative degradation to *diethylalloxantin*, $C_{12}H_{14}O_8N_4,H_2O$, large, transparent crystals, m. p. 209°, and 1-*ethylalloxan*, $C_6H_6O_4N_2,H_2O$, slender needles, m. p. 103° (decomp.); the latter substance is transformed by hydroxylamine hydrochloride into the previously described 1-ethylvioluric acid. Two of the ethyl groups of the triethyluric acid must therefore be present in the glyoxalone ring, that is, in positions 7 and 9, whilst the third must occupy position 3, since the alkylated compound is prepared from the solid potassium salt. As recorded by Drygin, when 3 : 7 : 9-triethyluric acid is warmed with concentrated hydrochloric acid, an ethyl group is eliminated as ethyl chloride and 3 : 7-*diethyluric* acid, slender, rhombic leaflets, m. p. 350—355°, is almost quantitatively produced; the same change occurs under the conditions of Zeisel's alkoxy determination. The presence of an ethyl group in position 3 is proved by oxidation of the acid to diethylalloxantin and ethylalloxan, m. p. 103°, whilst the second ethyl group necessarily occupies position 7, since fission of the acid with concentrated hydrochloric acid at 170° leads to the production of ethylglycine hydrochloride, which is identified by transforming it into 1-ethylhydantoin. 3 : 7 : 9-Triethyluric acid is readily converted by diazomethane in ethereal solution in the presence of a little water into 1-*methyl*-3 : 7 : 9-*triethyluric acid*, long, colourless needles, m. p. 104°. 1 : 3 : 7 : 9-*Tetraethyluric acid*, aggregates of slender needles, m. p. 82°, is prepared similarly with the aid of diazoethane. Treatment of the tetra-alkyl compounds with concentrated hydrochloric acid leads to the production of 1-*methyl*-3 : 7-*diethyluric acid*, feathery aggregates of needles, m. p.

257—258°, and 1 : 3 : 7-*triethyluric acid*, colourless needles, m. p. 218—219°. H. W.

The Beckmann Transformation. II. J. MEISENHEIMER and W. LAMPARTER (*Ber.*, 1924, **57**, [*B*], 276—282).—Reasons have previously been advanced (Meisenheimer, A., 1922, i, 152) in favour of a redistribution of formulæ among the benzildioximes whereby the α-dioxime receives the *anti*-, the β-dioxime the *syn*-, and the γ-dioxime retains the *amphi*-configuration. The tendency of the dioximes to lose water has been examined by heating in evacuated tubes at 155°; under these conditions, the α-dioxime is volatilised most slowly and with partial isomerisation to the β-dioxime; the latter sublimes more readily without undergoing decomposition, whereas only the γ-dioxime loses water and forms an anhydride; transformation into the β-dioxime accompanies the latter action and the formation of the anhydride ceases as soon as the isomerisation is complete. The behaviour of the oximes themselves is in harmony with that of their acetates, since the derivatives of the α- and β-forms are hydrolysed by cold sodium hydroxide solution to the corresponding oximes, whereas the diacetate of the γ-variety yields the anhydride. The behaviour of the dibenzoates exactly resembles that of the diacetates. The observations necessitate a new conception of the mechanism of anhydride formation, that represented in the following scheme being suggested:

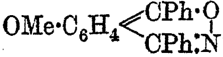


Dibenzoyl-α-benzildioxime, prepared from the α-dioxime and benzoyl chloride in the presence of pyridine, crystallises in colourless needles, m. p. 220°; *dibenzoyl-β-benzildioxime*, m. p. 157—158°, and *dibenzoyl-γ-benzildioxime*, m. p. 135°, are described. Benzoyl-α-benzilmonoxime, m. p. 96°, is obtained from the α-oxime and benzoic anhydride at 60—70°; it is reduced by zinc dust and glacial acetic acid to deoxybenzoin and, in this respect, it resembles the α-oxime. It is therefore regarded as a simple derivative of the latter and not as *ON*-dibenzoyl*iso*benzamide, OBz·CPh:NBz (cf. Werner and Piguet, A., 1905, i, 66; Meisenheimer, *loc. cit.*). Acetyl-α-benzilmonoxime, m. p. 67—68°, can be prepared from the α-monoxime and acetyl chloride in pyridine solution.

The conversion of diacetyl-β-benzildioxime, m. p. 124—125°, when heated above its melting point into a product, m. p. 148°, is accompanied by very slight loss in weight. When hydrolysed by sodium hydroxide, the latter substance gives mainly β-benzildioxime mixed with traces of the anhydride; it is therefore regarded as a dimorphous form of the ordinary diacetyl-β-benzildioxime containing small quantities of diacetyl-γ-benzildioxime.

δ-Benzildioxime (cf. Atack and Whinyates, T., 1921, **119**, 1184) is shown (cf. Brady and Dunn, this vol., i, 292) to be a mixture of much α- with little β-dioxime. H. W.

The Beckmann Transformation. III. J. Meisenheimer and H. Lange (*Ber.*, 1924, **57**, [*B*], 282—289).—A continuation of previous work (Meisenheimer, A., 1922, i, 152).

3 : 5-*Diphenyl*-4-p-*anisyl*isooxazole,  $OMe\cdot C_6H_4<\begin{matrix}CPh\cdot O\\ CPh{:}N\end{matrix}$, m. p. 189° (cf. Meisenheimer and Weibezahn, A., 1922, i, 176), prepared by the action of boiling sodium hydroxide solution on α-nitro-4-4-methoxystilbene, is converted by ozone in the presence of carbon tetrachloride into *benzoyl*-β-4′-*methoxybenzil*-7-*oxime*,

$$OMe\cdot C_6H_4\cdot CO\cdot C(Ph){:}N\cdot OBz,$$

colourless, prismatic plates, m. p. 95·5—96·5°, the configuration of which is thus established. This compound is also produced by the benzoylation of the 4′-methoxybenzil-7-oxime obtained by Meisenheimer and Jochelson (A., 1907, i, 858) from α-nitro-*p*-methoxystilbene; on hydrolysis, it gives the β-oxime and benzoic acid. The oxime is therefore the β-compound. This conclusion is confirmed by the observation that the oxime is converted by phosphorus pentachloride in the presence of ether into *anisoylformanilide*, $OMe\cdot C_6H_4\cdot CO\cdot CO\cdot NH\cdot Ph$, slender, yellow needles, m. p. 106—107° (the synthesis of which from anisoylformic acid is described). *Acetyl*-β-4′-*methoxybenzil*-7-*oxime*, obtained from the β-oxime and boiling acetic anhydride, forms coarse crystals, m. p. 85—86°.

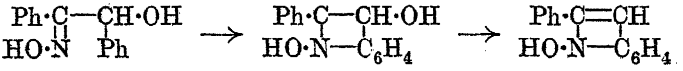
α-4′-*Methoxybenzil*-7-*oxime*, slender, colourless needles, m. p. 87·5—89°, is prepared by the action of amyl nitrite and sodium ethoxide on *p*-methoxydeoxybenzoin or (better) by treatment of 4′-methoxybenzil-7-oxime-7 : 7′-dimethylacetal,

$$OMe\cdot C_6H_4\cdot C(OMe)_2\cdot CPh{:}N\cdot OH$$

(cf. Meisenheimer and Jochelson, *loc. cit*), with boiling glacial acetic acid. *Acetyl*-α-4′-*methoxybenzil*-7-*oxime*, prepared from the oxime and boiling acetic anhydride, forms coarse, colourless crystals, m. p. 133—134°. *Benzoyl*-α-4′-*methoxybenzil*-7-*oxime*, obtained by benzoylation of the parent substance in the presence of pyridine or from the α-oxime and benzoic anhydride at 40—50°, crystallises in slender, colourless needles, m. p. 137·5—138·5°; it is converted by aqueous-alcoholic sodium hydroxide solution into benzonitrile and benzoic and anisic acids. α-4′-*Methoxybenzil*-7-*oxime methyl ether*, colourless, transparent plates, m. p. 62—63°, is isomerised to the methyl ether of the β-oxime by protracted treatment with hot, concentrated hydrochloric acid.

The view of Meisenheimer and Heim (A., 1907, i, 858) that 4′-methoxybenzil-7-oxime-7′ : 7′-dimethylacetal belongs to the α-series is confirmed by the observations that its methyl ether and *benzoyl* derivative (colourless needles or prisms, m. p. 127—128° dependent on the rate of heating) are converted by glacial acetic acid into the α-oxime or its derivatives, and that the oxime, when dissolved in glacial acetic acid and acetic anhydride, is converted by hydrogen chloride into benzonitrile and anisic acid. H. W.

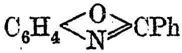
The Beckmann Transformation. IV. J. Meisenheimer and H. Meis (*Ber.*, 1924, **57**, [*B*], 289—297).—In connexion with the new conception of the course of the Beckmann transformation (cf. Meisenheimer, A., 1922, i, 152), the behaviour of a number of ortho-substituted benzophenoneoximes has been examined. Although not conclusive in any case, the results generally favour the authors' views. The only case recorded in the literature in which the stereochemical configuration of an oxime is definitely established and harmonises with the older conception of the Beckmann transformation is that of benzoin-α-oxime, which, according to Fischer and Hütz (A., 1895, i, 371), is converted by concentrated sulphuric acid into a derivative of indole, whereas the β-oxime does not behave in this manner. Doubts as to the constitution of the product have been expressed by Fischer (A., 1896, i, 696), but the definite proof that it is not 2-phenylindoxyl is afforded by the synthesis of the latter (Kalb and Bayer, A., 1912, i, 727) and its non-identity with the product obtained by Fischer and Hütz. Loss of water from benzoin-α-oxime must therefore occur in accordance with the scheme:

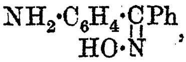
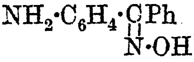


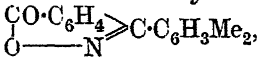
$$\begin{array}{l}\mathrm{Ph\cdot C{-}CH\cdot OH}\\ \mathrm{HO\cdot N\quad Ph}\end{array} \longrightarrow \begin{array}{l}\mathrm{Ph\cdot C{-}CH\cdot OH}\\ \mathrm{HO\cdot N{-}C_6H_4}\end{array} \longrightarrow \begin{array}{l}\mathrm{Ph\cdot C{=}CH}\\ \mathrm{HO\cdot N{-}C_6H_4}\end{array}$$

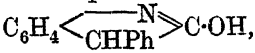
which necessitates a transposition of the configurations assigned previously to the α- and β-oximes. The modified conception of the course of the reaction explains the inability of deoxybenzoinoxime or phenylacetaldoxime to give a derivative of indole and the conversion of methylbenzoinoxime and benzoinoxime into the same product. The observation that acetyl-β-benzoinoxime can be oxidised to acetyl-β-benziloxime establishes the relationship between the benzoin- and benzil-oximes, which are thereby brought into complete harmony with one another.

o-Benzoylbenzoic acid is converted by hydroxylamine into an oxime-anhydride, $\begin{array}{l}\mathrm{CPh{=}N}\\ \mathrm{C_6H_4\cdot CO}\end{array}\!\!>\mathrm{O}$, m. p. 163—164°, which is unaffected by the customary reagents of the Beckmann change but is converted by concentrated sulphuric acid into phthalanil, whereby the oximino oxygen atom changes place with the oppositely situated phenyl radical. *o*-Chloro- and *o*-bromo-benzophenoneoximes lose halogen acid when treated with concentrated sodium hydroxide solution and yield the compound $\mathrm{C_6H_4}{<}\begin{array}{c}\mathrm{CPh}\\ \mathrm{O}\end{array}{>}\mathrm{N}$, thus rendering the configuration $\begin{array}{l}\mathrm{Br\cdot C_6H_4\cdot C\cdot Ph}\\ \quad\quad\;\;\mathrm{HO\cdot N}\end{array}$ probable. When treated with ether and phosphorus pentachloride they are converted into *o*-chloro- and *o*-bromo-benzanilide; benzoic *o*-chloro(*o*-bromo)-anilide is not produced, as would be expected from an oxime of the proposed configuration in accordance with the older view of the Beckmann transformation. For analogous reasons, the *syn*-configuration is assigned to the only known form of *o*-hydroxybenzophenoneoxime; it is converted by phosphorus pentachloride into salicylanilide accompanied by small amounts of anhydrobenzoyl-

o-aminophenol,  $C_6H_4{<}{}^{O}_{N}{>}CPh$, which can be derived only from the stereoisomeric oxime.

o-Aminobenzophenoneoxime exists in two stereoisomeric forms,  $\begin{matrix}NH_2\cdot C_6H_4\cdot CPh\\ \|\\ HO\cdot N\end{matrix}$, m. p. 156°,  $\begin{matrix}NH_2\cdot C_6H_4\cdot CPh\\ \|\\ N\cdot OH\end{matrix}$, m. p. 126°, the configurations of which are deduced from their behaviour when diazotised. The oxime of higher melting point is transformed by phosphorus pentachloride into the anilide of anthranilic acid, whereas crystalline products are not isolated from the isomeride of lower melting point.

2 : 4-Dimethylbenzophenone-2′-carboxylic acid gives only a single *oxime-anhydride*,  $\begin{matrix}CO\cdot C_6H_4\\ |\\ O\text{———}N\end{matrix}{>}C\cdot C_6H_3Me_2$, cubic crystals, m. p. 133—134°, which is transformed by concentrated sulphuric acid into 1 : 2 : 4-xylidine and phthalic acid. *Methyl* 2 : 4-*dimethylbenzophenone-2′-carboxylate*, coarse, colourless crystals, m. p. 69—70°, b. p. 209—210°/10 mm., could not be caused to react with hydroxylamine.

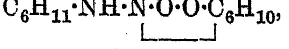
Mandelanilide is transformed by concentrated sulphuric acid at the ordinary temperature into *phenyloxindole*,  $C_6H_4{<}\begin{matrix}\text{———}N\\ CHPh\end{matrix}{>}C\cdot OH$, colourless, cubic crystals, m. p. 185—187°, but the yields are poor in consequence of simultaneous sulphonation. Mandel-*p*-toluidide, on the other hand, is converted quantitatively into 5-*methyl*-3-*phenyloxindole*, m. p. 211°. H. W.

p-Nitrobenzeneazopyrogallol (Chrome Brown P.A.). P. JUILLARD (*Mon. Sci.*, 1924, **14**, 25—27).—An account of work already published (A., 1923, i, 1139). E. H. R.

Symmetrical Di*cyclo*hexylhydrazine and Related Compounds. H. H. HARKINS and H. L. LOCHTE (*J. Amer. Chem. Soc.*, 1924, **46**, 450—455).—The authors have investigated the reduction of *cyclo*hexylideneazine by Skita's method. In no experiment did they obtain the unsymmetrical di*cyclo*hexylhydrazine described by Kijner and Beloff (A., 1911, i, 678).

s-*Di*cyclo*hexylhydrazine* (*hydrazo*cyclo*hexane*) (*hydrochloride*, white needles, m. p. 271° [corr.]) is very unstable in air, and has m. p. 6—10°; b. p. 260—270°/740 mm.; d_4^{27} 0·9384; n_D^{33} 1·4888. The crystalline *oxalate* and unstable *nitroso* derivative are also described.

*Azo*cyclo*hexane*, $C_6H_{11}\cdot N\colon N\cdot C_6H_{11}$, from di*cyclo*hexylhydrazine by oxidation with bromine water, forms straw-coloured needles, m. p. 34·5°. By hydrolysis of the azo compound with hydrochloric acid, *cyclo*hexylhydrazine (Kijner, *loc. cit.*) is obtained; the thioureide has m. p. 148°, instead of 143° (Kijner); the *benzylidene* compound $(C_6H_{11}\cdot N\cdot N\colon CHPh)_2CHPh$, colourless needles, has m. p. 183° (corr.). cyclo*Hexanone* cyclo*hexylhydrazone peroxide*,



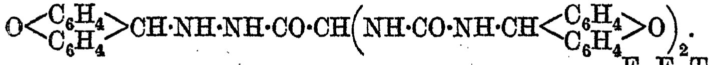
$$C_6H_{11}\cdot NH\cdot \underline{N\cdot O\cdot O\cdot C_6H_{10}},$$

is formed by the interaction of equivalent amounts of *cyclo*hexylhydrazine and *cyclo*hexanone. It crystallises in fine, white needles, m. p. 76° (decomp.), or when slowly heated, 74°. In contact with air it changes into an oil and a crystalline *substance*, m. p. 136—137°, neither of which has been identified. Attempts to obtain the free *cyclo*hexanone *cyclo*hexylhydrazone in the solid form failed.

Attempts to reduce di*cyclo*hexyl nitrosoamine to as.-di*cyclo*hexylhydrazine by Fischer's method were unsuccessful. A. B. S.

Action of Hydrazine on Hydantoin and Allantoin. R. Fosse, P. Hagène, and R. Dubois (*Compt. rend.*, 1924, **178**, 578—581).—Hydrazine hydrate converts hydantoin, at the ordinary temperature, into hydantoylhydrazide (A., 1923, i, 938). Hydantoylhydrazide affords sparingly soluble crystalline precipitates with aqueous solutions of benzaldehyde and anisaldehyde. *Benzylidenehydantoylhydrazone*, $CHPh{:}N\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot CO\cdot NH_2$, has m. p. 206—209° (decomp. and varying with rate of heating); p-*methoxybenzylidenehydantoylhydrazone* becomes coloured at 215—220° and melts at 220—227°, the temperatures varying with rate of heating.

Allantoin is converted by hydrazine into the *monohydrate* of *allantoylhydrazide*, $NH_2\cdot NH\cdot CO\cdot CH(NH\cdot CO\cdot NH_2)_2,H_2O$. The anhydrous hydrazide has m. p. 185° (decomp.). Allantoylhydrazide (1 mol.) condenses with xanthhydrol (3 mols.) to give a *substance* (annexed formula), having m. p. 223—225° (decomp.).



$$O{<}\substack{C_6H_4\\C_6H_4}{>}CH\cdot NH\cdot NH\cdot CO\cdot CH\left(NH\cdot CO\cdot NH\cdot CH{<}\substack{C_6H_4\\C_6H_4}{>}O\right)_2.$$

E. E. T.

Additive Products of the Phosphineimines. M. Masriera (*Anal. Fís. Quím.*, 1924, **22**, 25—48; cf. this vol., i, 234).—A continuation of earlier work on the additive compounds derived from phosphineimines. Acetylphenylchloroamide gives with triphenylphosphine an additive *compound*, probably $Cl\cdot PPh_3\cdot NPhAc$, which is thought to be isomeric with the unstable compound formed from triphenylphosphinephenylimine and acetyl chloride. It is stable in air and forms white tablets having m. p. 109°. Triphenylphosphine and *p*-toluenesulphonephenylchloroamide gives a compound identical with that obtained from toluene-*p*-sulphonyl chloride and triphenylphosphinephenylimine. 2 : 4-*Dichlorophenyl azide* (obtained by the action of sodium nitrite and hydrochloric acid on 2 : 4-*dichlorophenylhydrazine hydrochloride*, white needles, m. p. 205—208° [decomp.]), forms yellow needles, m. p. 51°, and is explosive when dry. With triphenylphosphine in ethereal solution it affords *triphenylphosphine*-2 : 4-*dichlorophenylimine*, $PPh_3{:}N\cdot C_6H_3Cl_2$, white tablets, m. p. 161°. The last substance is not basic and does not give an additive compound with toluene-*p*-sulphonyl chloride Triphenylphosphine and *p*-toluenesulphone-2 : 4-dichlorophenylchloroamide give an unstable additive *compound*. Various methods for the *N*-chlorination of anilides are studied. G. W. R.

Intensely Coloured Sodium Triphenylboryl, a remarkable Analogue of Sodium Triphenylmethyl. E. Krause (*Ber.*, 1924, **57**, [*B*], 216—217).—A preliminary communication. Ethereal solutions of boron triphenyl (Krause and Nitsche, A., 1922, i, 694) become intensely coloured in the presence of sodium wire and ultimately deposit orange-yellow, prismatic crystals. The coloured solutions are immediately decolorised by oxygen. H. W.

Organo-chromium Compounds. IV. Chromium Tetraphenyl Hydroxide. F. HEIN and O. SCHWARTZKOPFF (*Ber.*, 1924, **57**, [*B*], 8—14; cf. A., 1921, i, 826; 1922, i, 76, 77).—*Chromium tetraphenyl hydroxide*, $CrPh_4{\cdot}OH,3H_2O$, is prepared by the action of silver oxide on chromium tetraphenyl iodide dissolved in moist chloroform or methyl alcohol, or by the electrolysis of a solution of the iodide in alcohol with a platinum or mercury cathode and rotating silver anode. It crystallises in orange leaflets, m. p. 104—105°, and resembles closely the corresponding pentaphenyl derivative. Measurements of its electrolytic conductivity in aqueous solution show that it is comparable with the alkali hydroxides in strength, whilst comparative experiments in methyl-alcoholic solution show it to be a stronger base than chromium pentaphenyl hydroxide. The base is converted into the corresponding iodide, bromide, and chloride, and into chromium tetraphenylchromitetrathiocyanatodiammine, $Ph_4Cr\left[Cr\genfrac{}{}{0pt}{}{(CNS)_4}{(NH_3)_2}\right]$, which are identical with the compounds obtained previously (with elimination of a phenyl group) from chromium pentaphenyl hydroxide (cf. A., 1922, i, 76). *Chromium tetraphenyl hydrogen carbonate*, $CrPh_4{\cdot}HCO_3,2H_2O$, forms orange crystals, m. p. 110—111°. *Chromium tetraphenyl dianthranilate*, $NH_2{\cdot}C_6H_4{\cdot}CO_2CrH{\cdot}Ph_4$, orange needles, m. p. 145—146°, and the *salt*,

$$NH_2{\cdot}C_6H_4{\cdot}CO_2CrHPh_4,NH_2{\cdot}C_6H_4{\cdot}CO_2H,$$

m. p. 130°, are also described. H. W.

Structure of Proteins. E. ABDERHALDEN and W. STIX (*Z. physiol. Chem.*, 1923, **132**, 238—250).—With the view of differentiating between dipeptides and the corresponding diketopiperazines the formyl and acetyl derivatives of these compounds have been investigated. *Diformylglycine anhydride* crystallises in rosettes, m. p. 112° (not sharp). A formyl derivative of leucylglycine anhydride could not be prepared. Diacetylglycine anhydride was obtained crystalline (cf. Franchimont and Friedmann, A., 1908, i, 509), also *diacetylglycylalanine anhydride* (m. p. 47°, not sharp) but the *acetyl* derivative of *leucylglycine anhydride* could be obtained only as a syrup. *Diacetyl-leucylglycine* was obtained as a yellow powder (m. p. 95°) by the action of acetyl chloride on the dipeptide. An attempt to prepare bisulphite derivatives of glycine anhydride and silk peptone was unsuccessful. By the reduction of glycine anhydride, alanylglycine anhydride, and leucylglycine anhydride with metallic sodium in ethyl or amyl alcohol, small yields of the corresponding piperazines were obtained. *Dibenzoylmethylpiperazine*, $C_5H_{10}N_2Bz_2$ (crystallising in small plates), and *methylpiperazine dihydrochloride* were prepared from methylpiperazine obtained by reduction of alanylglycine anhydride. The reduction of diacetylglycine anhydride, diacetylglycylalanine anhydride, and diacetyl-*dl*-leucylglycine anhydride yielded piperazines, whilst from *dl*-leucylglycine and glycyl-*d*-alanine subjected to the same reaction the unchanged compounds were obtained. On applying the method to silk peptone, a mixture of piperazines was obtained yielding crystalline picrates and platinum salts, but these were not further characterised. It is hoped to extend the method to decide whether or not diketopiperazines are present as such in the protein molecule. J. P.

Effect of Ultra-violet Rays on Protein Solutions. R. MOND (*Pflüger's Archiv*, 1923, **200**, 374—378; from *Chem. Zentr.*, 1924, i, 69; cf. A., 1923, i, 868).—Solutions of crystalline egg-albumin or serum-albumin having p_H greater than 4·6 are rendered more acid by ultra-violet radiation, whilst solutions with p_H less than 4·3 are rendered more alkaline. The acidity of suspensions of lecithin is appreciably increased. Sera subjected to radiation have no hæmolytic effect and no effect on an isolated frog's heart. It is supposed that radiation causes the development in sera of substances which exert a dilatory effect on the vascular system. G. W. R.

New Sulphur-containing Amino-acid Isolated from the Hydrolytic Products of Protein. II. Sulphur Excretion after Ingestion. J. H. MUELLER (*J. Biol. Chem.*, 1923, **58**, 373—375).—When the amino-acid $C_5H_{11}O_2NS$ (cf. A., 1923, i, 869) is ingested by man, the sulphur which it contains is excreted in the urine in the form of inorganic sulphate. This is further evidence in favour of the view that the compound is a primary cleavage product of proteins. E. S.

Lysolecithins and Lysocephalins. II. Isolation and Properties of Lysolecithins and Lysocephalins. P. A. LEVENE, I. P. ROLF, and H. S. SIMMS (*J. Biol. Chem.*, 1924, **58**, 859—871; cf. A., 1923, i, 650).—The mixture of lysocephalin and lysolecithin, resulting from the action of cobra venom on egg yolk, has been separated by fractional crystallisation from chloroform and ether after precipitation with cadmium chloride. Lysocephalin has m. p. 198° (decomp.) and $[\alpha]_D^{35}+2{\cdot}0°$ in glacial acetic acid; lysolecithin, which is much more soluble in solvents, softens at about 100°, decomposes at 263°, and has $[\alpha]_D^{20}-2{\cdot}6°$ in chloroform, and $[\alpha]_D^{35}+0{\cdot}8°$ in glacial acetic acid. Hydrolysis yielded palmitic and stearic acids, whereas lysocephalin only yielded stearic acid. Dissociation constants were found, for lysolecithin $K_1=0{\cdot}18$, $K_2=1{\cdot}3\times10^{-12}$, and the isoelectric range p_H 2·75—9·90; for lysocephalin $K_1=3\times10^{-4}$, $K_2=3{\cdot}4\times10^{-10}$ and isoelectric range p_H 5·5—7·5. The question as to which of these constants is the acid and which the basic one is discussed. The hæmolytic activity of lysolecithin was found to be three times that of lysocephalin. G. M. B.

The Carbohydrate Group of Thymonucleic Acid. H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1924, **132**, 297—300).—Thymonucleic acid on being hydrolysed and steam distilled yields a distillate which gives a red fuchsin-sulphite reaction, a green coloration with pine shavings, a red coloration with aniline acetate, and with orcinol–hydrochloric acid an intense reddish-violet product soluble in amyl alcohol. The ethereal extract of the hydrolysate gives the same reactions. The reactions formerly regarded as being those of a glucal-like residue are therefore ascribed to a volatile, ether-soluble substance which is regarded as furfuraldehyde. No definite conclusions are drawn as to the nature of the sugar residue responsible for the furfuraldehyde reactions. J. P.

Biochemistry.

Carbon Dioxide Absorption Curve of Human Blood. IV. Relation of the Hæmoglobin Content of Blood to the Form of the Carbon Dioxide Absorption Curve. V. The Construction of the CO_2 Absorption Curve from One Observed Point. VI. The Relationship of the CO_2 of Blood to that of Plasma. J. P. Peters, H. A. Bulger, and A. J. Eisenman (*J. Biol. Chem.*, 1924, **58**, 747—768, 769—771, 773—791).—IV. From a number of determinations of the carbon dioxide content of blood and its "true" plasma at various values of P_{CO_2} (*ibid.*, 1923, **55**, 687, 709), the relation of the hæmoglobin content of human blood to the slope of the absorption curve has been studied. The assumption (Van Slyke, Hastings, and Neill, A., 1923, i, 163) that values of individual buffers occurring in a complex system such as blood, when measured by the ratio $\Delta[MHCO_3]/\Delta P_H$ (Van Slyke, A., 1922, i, 893), can be considered as simple additive functions is shown to be unwarranted. Under the restricted conditions of the experiments recorded, the simple difference in the values of blood carbon dioxide content at P_{CO_2} 60 and 30 mm. (written $\Delta[CO_2]_{60-30}$) is a satisfactory and practical measure of buffer. From the scanty data available it seems possible that the buffer values of individual constituents, or at least the two main phases of the blood, when estimated as $\Delta[CO_2]_{60-30}$, may be considered as simple additive functions.

V. The determinants of the slope of the carbon dioxide absorption curve, other than the hæmoglobin concentration, have not yet been completely ascertained, but a method of calculation is now given which allows for this factor. In the relation $\Delta[CO_2]_{60-30}=0{\cdot}334 \times$ (oxygen capacity)$+6{\cdot}3$, cell volume may be substituted for oxygen capacity by means of the further equation: (oxygen capacity)$=$ 0·464 (cell volume) where both are expressed in vols. %. By the use of these relations, together with the graphic logarithmic method previously described (A., 1923, i, 1249), it is possible to construct the absorption curve from any single point. The average deviation of $\Delta[CO_2]_{60-30}$ from the mean in the experiments recorded is 0·5 vol.%

VI. Determinations are recorded of oxygen capacity (h), cell volume, and carbon dioxide content of whole blood $[CO_2]_b$, and of the carbon dioxide content $[CO_2]_p$ of the plasma at $P_{CO_2}=40$ mm. on a number of specimens of blood, and on others at $P_{CO_2}=30$ and 60 mm. The relation $[CO_2]_p=[CO_2]_b+(0{\cdot}0159[CO_2]_b-0{\cdot}281)h$ is found to hold when $P_{CO_2}=40$ mm. and allows of the calculation of the carbon dioxide content of plasma from that of whole blood. For tensions other than 40 mm., a slightly modified relation is used. G. M. B.

Rates of Reduction and Oxidation of Blood. A. E. KOEHLER (*J. Biol. Chem.*, 1924, **58**, 813—830).—The rate of oxidation and reduction of blood was followed by comparison with fully oxygenated blood in a colorimeter so designed as to allow of rotation of the specimen in a stream of gas. The velocity of the reactions was found to be largely affected by the oxygen tension. An increase of p_H increases the rate of oxidation and depresses the rate of reduction, whilst a decrease of p_H has the opposite effects. The influence of carbon dioxide or lactic acid on the velocities is in accordance with the changes of p_H produced, there being no specific action of carbon dioxide. Certain ions such as $Na^\cdot$ modify the oxidation and reduction curves considerably. G. M. B.

Cholesterol and Bicarbonate Content of Blood in Experimental Kidney Diseases. A. STASIEK (*Biochem. Z.*, 1924, **144**, 477—481).—Hypercholesterinæmia can be produced in dogs by inducing kidney disease by such drugs as cantharidine, uranium nitrate, and mercuric chloride. As the animals were fed during the experimental period on diets free from fat and cholesterol it may be assumed that the hypercholesterinæmia is of endogenous origin. Acidosis is not responsible for this metabolic derangement, since the bicarbonate content of the blood remains normal until after the manifestation of the hypercholesterinæmia. It is suggested that this condition is produced, not only because of the damage done to the cells of the kidney by the above agents, but also by the effect of these agents on the lipoids in other parts of the body. S. S. Z.

Amino-acid Content of the Blood in Normal and Pathological Conditions. C. H. GREENE, K. SANDIFORD, and H. ROSS (*J. Biol. Chem.*, 1924, **58**, 845—857).—The amino-nitrogen content of blood as determined by the Folin method (which was found to be trustworthy in presence of an excess of urea) in cases of twenty different pathological conditions was similar to that in the blood of normal persons, namely, between 4·8 and 7·8 mg. per 100 c.c., with an average of 6·3 mg. The level of amino-nitrogen may be increased by flooding the organism with amino-acids during digestion or from the rapid autolysis of body-tissue, but otherwise deviation beyond the limits mentioned is rare. G. M. B.

Effect of Adrenaline on the Composition of Blood under Normal Conditions in Fasting, and in Avitaminosis. D. ALPERN and J. A. COLLAZO (*Z. ges. exp. Med.*, 1923, **35**, 288—295; from *Chem. Zentr.*, 1924, i, 67—68).—Residual nitrogen, urea, sugar, and amino-acids in the blood of fasting dogs were found to be scarcely above normal. Values appreciably above the normal were obtained with a diet poor in vitamins. The total ethereal extract of blood was depressed in fasting, but increased by a diet low in vitamins. Adrenaline hyperglycæmia was less marked with low-vitamin diet than in fasting. This was the case even with a triple dose of adrenaline. In the case of fasting and normally-fed animals, the administration of adrenaline resulted in a decrease in the total ether extract and the total ethyl alcohol extract of the blood. With a diet poor in vitamins, on the other hand, increases in these values were observed. The adrenaline effect is related to the diminished power of oxidation and assimilation in the body-cells in avitaminosis. G. W. R.

Formation of Methæmoglobin. W. Lipschitz and J. Weber (*Z. physiol. Chem.*, 1924, **132**, 251—274).—The influence of various aromatic and other compounds in converting the blood pigment into methæmoglobin has been investigated. β-Phenylhydroxylamine, hydrazobenzene, and arsenic hydride form methæmoglobin only in the presence of oxygen and have no action on reduced hæmoglobin. Dimethylaminophenyl ether, azo- and azoxy-benzene, and *p*-hydroxyazobenzene are without effect on hæmoglobin. Benzoquinone and its oximes are decreasingly active in forming methæmoglobin in the order given, but quinonechlorimine is five times as active as quinone. Hæmoglobin at 20° brings about a catalytic decomposition of hydroxylamine into nitrogen and ammonia which reaches a maximum when the reactants are present in the proportion 2 mols. of hydroxylamine : 1 mol. of hæmoglobin. Methæmoglobin catalyses the same reaction. Whilst hydroxylamine and α-methylhydroxylamine convert both oxyhæmoglobin and reduced hæmoglobin into methæmoglobin, β-phenylhydroxylamine acts on oxyhæmoglobin only, and when present in excess converts methæmoglobin into reduced hæmoglobin. By treating reduced hæmoglobin with arsenic hydride followed by a little oxygen a, pigment is obtained with a band at 608—625 $\mu\mu$, which on further treatment with oxygen yields methæmoglobin. This is in agreement with the "nitrobenzenehæmoglobin" described by Filehne (*Arch. exper. Path.*, 1878, **9**, 329), and the latter supposed pigment is therefore regarded as unspecific. J. P.

Formation of Porphyrin from Blood Pigment. I. Spectroscopic Properties of Porphyrin Esters. O. Schumm (*Z. physiol. Chem.*, 1924, **132**, 34—61).—By treatment of hæmoglobin free from oxygen, from blood corpuscles, with 25% hydrochloric acid, a porphyrin is formed. The same porphyrin is formed along with hæmatin if fuming hydrochloric acid is used. If, however, the hæmoglobin is treated with 1·3—2·6% of alcoholic hydrogen chloride, in the presence or in the absence of air, no formation of porphyrin occurs. A porphyrin, obtained from hæmatin by treatment with hydrazine hydrate, possesses properties and spectrum similar to those of the porphyrin obtained from hæmoglobin by the action of hydrochloric acid, but it has not been proved that they are identical. The spectroscopic properties of the methyl esters of urinoporphyrin

(Fischer), cotporphyrin, and of Nenki's hæmatoporphyrin are described. W. O. K.

Blood Pigment of *Arenicola*. J. Barcroft and H. Barcroft (*Proc. Roy. Soc.*, 1924, **B**, **96**, 28—42).—The blood pigment of *Arenicola* differs from human hæmoglobin in the following facts: (1) the α-absorption bands of the oxy and carboxy compounds are displaced towards the violet end of the spectrum; (2) its affinity for oxygen is much greater, so that gaseous exchange can take place at pressures of oxygen between 2 and 3 mm.; (3) carbon monoxide has only 70 times the affinity for *Arenicola* hæmoglobin that oxygen has (as compared with 250 times for human hæmoglobin). The function of the pigment is probably to act as a reserve store of oxygen for those periods during which the animal has not access to sea-water. C. R. H.

Inorganic Bases and Phosphates in Relation to the Protein of Blood and other Body Fluids in Bright's Disease and in Heart Failure. H. A. Salvesen and G. C. Linder (*J. Biol. Chem.*, 1923, **58**, 617—634).—Determinations have been made of the content of certain inorganic constituents (bases and phosphates) and of proteins in the blood plasma of patients suffering from Bright's disease. In the absence of uræmia, the content of calcium and of protein was found to run parallel. In uræmic cases, however, this parallelism was absent, a marked fall in the calcium content occurring with a protein content only slightly below normal; this effect is attributed to a great retention of phosphates in these cases.

From analyses of blood plasma and other body fluids in cases of heart failure, it appears that 55—70% of the serum calcium is diffusible. The non-diffusible calcium is probably bound to proteins. E. S.

Action of Peptone and of Nucleic Acids on the Coagulability of the Blood. J. W. Pickering and J. A. Hewitt (*Proc. Roy. Soc.*, 1924, **B**, **96**, 77—94).—Intravascular injection of Witte's peptone inhibits coagulation of the blood in tortoises which have been deprived of hepatic activity, and, to a variable extent, in rats and dogs. Addition of peptone to shed blood delays its coagulation if the blood has not been in contact with damaged tissue. Such blood contains fibrinogen, and will clot on dilution with water or on prolonged exposure to air. Similar results are obtained with nucleic acids derived from thymus and yeast. In all cases the anticoagulant effect is antagonised by the presence of increased amounts of carbon dioxide in the circulating blood; animals can be immunised against the nucleic acid effect by serial intravascular injections of protein-free nucleic acid preparations. C. R. H.

Equilibria involving Calcium, Hydrogen, Carbonate, Bicarbonate, and Phosphate Ions. I. N. Kugelmass and A. T. Shohl.—(See ii, 235.)

Physico-chemical Basis of Vital Permeability. IV. R. Brinkman and A. von Szent-Györgi.—(See ii, 235.)

Relation between Calcium and Protein of Serum in Tetany due to Parathyroidectomy. H. A. Salvesen and G. C. Linder (*J. Biol. Chem.*, 1923, **58**, 635—639).—The decrease in serum calcium in parathyroidectomised dogs is not accompanied by a decrease in plasma protein. Apparently, a parallelism between the decrease in calcium and protein (cf. preceding abstract) indicates a decrease in protein-bound calcium and does not lead to tetany, whereas a decrease in calcium without a corresponding decrease in protein (as in parathyroidectomy) indicates, primarily, a decrease in ionised calcium, which leads to tetany. E. S.

Mechanism of Syphilitic Serological Reactions. The Protein Fractions of Human Blood Serum. R. Stern (*Biochem. Z.*, 1924, **144**, 115—137).—A study has been made of the protein fractions of syphilitic and non-syphilitic sera. The so-called euglobulin fraction, comprising a small part of the water-insoluble globulin, has no significance for the typical serological reactions in syphilitic conditions. This is called " Labileglobulin." The separation from sera of a true euglobulin is described and this on peptisation in " Normosal " (Sächsischen Serumwerke) gives positive or negative Wassermann and Sachs-Georgi reactions according to the reaction of the original serum. The residual serum after removal of the euglobulin gives uniformly negative results, whether separated into its fractions or otherwise. The electrical charge of the euglobulin responsible for the specific reactions bears no relation to the positive or negative nature of the tests. Tannin solutions may convert negative into positive sera, and may themselves react positive to the Wassermann and Sachs-Georgi tests. It is tentatively suggested that the specific action of the euglobulin is due to dehydration in accord with the action of tannin in sensitising dyestuff sols. J. P.

Physiology of Digestion. I. The Diastatic Power of the Mixed Saliva of Man, the Horse, Ox, Pig, and Dog, with Observations on the Complex Nature of Salivary Diastase. II. Fluctuations in the Diastatic Power of Mixed Saliva. C. Schwarz and K. Steinmetzer (*Fermentforsch.*, 1924, **7**, 229—253).—I. For man the mean diastatic power (D) found was 1600, for the pig only 14. The saliva of the other animals contained no amylase. Amylase exists in the human salivary glands as an inactive proferment which becomes active upon secretion under the influence of the salts (possibly sodium chloride) of the saliva. II. The diastatic power of human saliva becomes constant in the fasting state. R. K. C.

Physiology of Digestion. X. The Effect of Kristallose, Saccharin, and Parasaccharin on Salivary Diastase. C. Schwarz and E. Buchlman (*Fermentforsch.*, 1924, **7**, 282—300). **XI. The Effect of Kristallose, Saccharin, and Parasaccharin on Peptic and Tryptic Digestion.** C. Schwarz and V. Zellinger (*ibid.*, 301—306).—X. These substances have no effect on salivary diastase in concentrations up to 1%. Earlier results to the contrary are due to failure to control the p_H of the tests. XI. In concentrations such as might be taken by man, these are without effect on protein digestion by pepsin or trypsin. ("Kristallose" is the sodium salt of saccharin.) R. K. C.

Physiology of Digestion. VIII. Digestion in the Crop of the Fowl. C. SCHWARZ and H. TELLER (*Fermentforsch.*, 1924, **7**, 254—269).—The secretion of the crop is a yellow, viscid fluid generally acid to litmus but devoid of amylolytic or proteolytic activity. Lactic acid is generally to be found in the crop contents, but free hydrochloric acid is absent. Food remains many hours in the crop whilst it undergoes swelling (and some autofermentation) preparatory to digestion elsewhere. No absorption of water, salt, or dextrose by the mucous membrane of the crop was detected. R. K. C.

Absorption of Lecithin. F. EICHHOLTZ (*Biochem. Z.*, 1924, **144**, 66—69).—Lecithin (Witte) fed to young dogs produced an increase in the alcohol-ether-soluble organic phosphorus compounds of the blood, but had no effect on the total fat. It is concluded that lecithin is assimilated as such and that its fatty acid residue is not built up into neutral fats. J. P.

Digestion Experiments with the Raw White of Egg. II. The Digestibility of Unbeaten in Comparison with Beaten Whites. M. S. ROSE and G. MACLEOD (*J. Biol. Chem.*, 1923, **58**, 369—371; cf. *ibid.*, 1922, **50**, 83).—In general, the digestion of beaten egg whites is somewhat more complete than that of unbeaten. The average coefficient of digestibility obtained for raw white of egg is 83%, and for cooked white of egg 86%. E. S.

Effect of Reaction Changes upon Human Carbohydrate and Oxygen Metabolism. J. B. S. HALDANE, V. B. WIGGLESWORTH, and C. E. WOODROW (*Proc. Roy. Soc.*, 1924, **B**, **96**, 15—28).—In the alkalosis produced by forced breathing or by ingestion of sodium bicarbonate the preliminary activation of glucose, which is necessary before it can be metabolised, is inhibited, with resulting acetonuria, and hyperglycæmia and glycosuria after less than half the normally tolerated dose of glucose.

The acidosis caused by breathing carbon dioxide has no effect on carbohydrate metabolism; after ingestion of ammonium chloride there is observed a lowering of sugar tolerance in the post-acidotic stage which is probably due to a failure of the glycogenic function of the liver.

Ingestion of sodium hydrogen carbonate causes an increase in the consumption of oxygen, the reverse effect being produced by ammonium chloride. C. R. H.

Clinical Calorimetry. XXXIV. Ketosis and the Respiratory Exchange in Diabetes. H. B. RICHARDSON and W. S. LADD (*J. Biol. Chem.*, 1924, **58**, 931—968).—The fatty acid : glucose ratio, calculated from the data obtained by the calorimetric method previously described (Richardson and Mason, *ibid.*, 1923, **57**, 587), was found to be parallel to the excretion of acetone compounds. The threshold of ketosis was found at a ratio of about 1·5 to 1, which corresponds with the presence, during oxidation, of 1 mol. of keto-acid for every mol. of glucose. This parallelism is evidence that the respiratory quotient in diabetes is a true measure of oxidation. Diabetic patients were often able to take diets containing a larger proportion of ketogenic substances than is called for by the above-mentioned molecular ratio, which indicates that the proportions of foodstuffs oxidised were not the same as those ingested.

The fall of ketosis observed in diabetic patients, when fasting, is accounted for by the simultaneous drop in the fatty acid : glucose ratio calculated from the calorimetric data. It was due primarily to a decrease in the total metabolism with a consequent diminution in the metabolism of fat and protein.

During fasting there was little or no increase in the total quantity of glucose oxidised when this was computed as being derived from protein and the glycerol of the fat, as well as from the carbohydrate, undergoing metabolism. Fasting reduces the blood-sugar chiefly by depleting the endogenous sources of glucose. There is often an increase in the oxidation of glucose during the subsequent period of restricted diet, but this is not necessarily due to the fast.

G. M. B.

Acetonæmia, especially in Avitaminosis. M. Händel (*Biochem. Z.*, 1924, **144**, 258—264).—Using a micro method based on that of Bang, the acetone content of the blood of normal, starving, phloridzinised, depancreatised, and avitaminosed dogs, and of normal ox and human blood, has been determined. Avitaminosis leads to no increase in the acetone compounds of dog's blood. Normal human blood contains only traces of free acetone, 2 to 4 mg.% as acetoacetic acid, and 3 to 5 mg.% as β-hydroxybutyric acid. Acetonæmia is most marked in depancreatised dogs and in dogs which have been simultaneously starved and phloridzinised. J. P.

Carbohydrate Metabolism. XXI. The Relation of Sugar Excretion to Renal Integrity. F. P. Underhill and G. Wilens (*J. Biol. Chem.*, 1923, **58**, 153—162).—Following experimental tartrate nephritis, the renal threshold for dextrose appears to be alternately raised and lowered. An injection of dextrose increases the hyperglycæmia. E. S.

Physiological Behaviour of Glucosan. J. Kerb. **Glucosan.** J. Kerb and E. Kerb-Etzdorf (*Biochem. Z.*, 1924, **144**, 60—63).—Arising from Grafe's treatment of diabetes with caramel (*Deutsch. Arch. f. klin. Med.*, 1914, **116**, 437) the physiological action of α-glucosan, *l*-glucosan, and lævulosan is under investigation. The administration of α-glucosan to diabetics and to depancreatised dogs does not produce a rise in blood-sugar. In one case of severe diabetes a slight decrease lasting for one hour was observed. J. P.

Some Changes in the Composition of Blood due to the Injection of Insulin. A. P. Briggs, I. Koechig, E. A. Doisy, and C. J. Weber (*J. Biol. Chem.*, 1924, **58**, 721—729).—A series of analyses of the blood of dogs after injection of insulin, show that the concentrations of glucose, inorganic phosphate, and potassium in the blood are thereby decreased. A parallel increase observed in the concentration of lactic acid present, is believed to be due to the influence of insulin on the reversible reaction : glucose $\rightleftharpoons$ lactic acid. G. M. B.

Insulin and Phloridzin Diabetes. T. P. NASH, jun. (*J. Biol. Chem.*, 1923, **58**, 453—462).—The results reported are of a preliminary nature and appear to indicate that the administration of insulin to a phloridzinised dog does not cause a utilisation of sugar. E. S.

Influence of Insulin on Phloridzin Diabetes. M. RINGER (*J. Biol. Chem.*, 1923, **58**, 483—501).—Injection of insulin into completely phloridzinised dogs causes the oxidation of dextrose. At the same time, deposition of dextrose as glycogen takes place, the protein metabolism and the heat production are reduced, and the excretion of ketonic substances ceases. These results indicate that the effect of phloridzin is due to a transitory injury to the pancreas. It is suggested that, using phloridzinised dogs, insulin might be assayed in terms of the utilisation of dextrose. The maximum utilisation (oxidation) obtained in the present experiments was 0·95 g. of dextrose per unit of insulin. E. S.

Effect of Alcoholic Pancreas Extract (Insulin) on the Behaviour of the Kidneys towards Dextrose. S. VAN CREVELD and E. VAN DAM (*Nederl. Tijdschr. Geneeskunde*, 1923, **67**, II, 1498—1510; from *Chem. Zentr.*, 1924, i, 215).—From experiments on the perfusion of frog kidneys with dextrose solutions after administration of insulin it is concluded that the specific substance of insulin has a direct effect on the kidneys. G. W. R.

What Substance in the Carbohydrate Metabolism is acted on by Insulin? E. TOENNIESSEN (*Z. physiol. Chem.*, 1924, **133**, 158—164).—The author maintains that insulin acts on the lactic acid formed in the metabolism of carbohydrates in the animal organism, since all the previous stages in this metabolic process proceed normally in the absence of the pancreas. He was able to demonstrate that on adding lactic acid to minced pancreas there is no increase in the formation of acetaldehyde, but in the presence of pancreas and minced muscle the amount of acetaldehyde formed was double that formed by the control organs alone. Acetaldehyde was also formed on introducing insulin into normal and more so into diabetic blood. It is supposed to be derived from lactic acid. S. S. Z.

Comparative Study of the Blood-sugar Concentration in the Liver Vein, the Leg Artery, and the Leg Vein during Insulin Action. C. F. CORI, G. T. CORI, and H. L. GOLTZ (*J. Pharm. Exp. Ther.*, 1923, **22**, 355—373).—Determinations of the blood-sugar show that in the rabbit, starved for twenty-four hours, the concentration in the liver vein is on the average 28 mg.% higher than in the neck vein, and 23 mg.% higher than in the femoral artery, whilst that in the femoral artery is 8 mg.% higher than that in the femoral vein. Under the influence of insulin, the first two figures tend to decrease and the last one to increase, so that there would appear to be diminished output of sugar by the liver, and increased uptake by the muscles. W. O. K.

Physiological Action of Insulin. U. Sammartino and D. Liotta (*Arch. Farm. Sperim.*, 1924, **23**, 13—46).—The authors discuss the question of glycæmia in relation to the action of insulin. The blood-sugar content of fasting rabbits following the injection of a unit dose of insulin falls below 0·045 mg.%, and is accompanied by hypoglycæmic convulsions and death. Even after death has been prevented by intravenous injection of dextrose (1 g. per kg. body weight), hypoglycæmia persists for 3—5 days. After repeated unit doses, recovery through injection of sugar is no longer possible. Administration of sucrose, or of dextrose in amount less than 1 g. per kg. body weight, does not prevent death from hypoglycæmia. Insulin also produces a fall in glycæmia in hyperglycæmia produced by adrenaline or lesion of the fourth ventricle. Hypoglycæmic coma and death are not prevented by administration of vaso-constrictive substances, such as ergotine and pituitary extract. Injection of insulin produces a lowering of blood pressure which cannot be neutralised by intravenous injection of sugar. G. W. R.

Glucokinin. III. An Apparent Synthesis in the Normal Animal of a Hypoglycæmia-producing Principle. Animal Passage of the Principle. J. B. Collip (*J. Biol. Chem.*, 1923, **58**, 163—208).—The marked hypoglycæmia and other symptoms which are produced in normal rabbits by the injection of glucokinin (A., 1923, i, 1247) have also been observed after injection of guanidine sulphate or of overdoses of insulin, and after prolonged fasting; hypoglycæmia also occasionally occurs spontaneously, in which case *Coccidia oviforme* have been found in the liver. Transitory relief of the symptoms may be effected by injection of dextrose, but the death of the animal ultimately results. When defibrinated blood or serum from such hypoglycæmic rabbits is injected into normal rabbits, similar symptoms occur, animal passage (rabbit) of the hypoglycæmia-producing principle apparently being capable of indefinite extension. The principle is thermostable, undergoes dialysis, and is precipitated from blood by ammonium sulphate, but not by tungstic acid. E. S.

Aqueous Extracts of Pancreas. II. Physical and Chemical Behaviour of Insulin. H. A. Piper, R. S. Allen, and J. R. Murlin (*J. Biol. Chem.*, 1923, **58**, 321—336).—Observations which have been made during the preparation of insulin lead to the conclusion that insulin is not a protein; it appears, however, to exist in the pancreas in combination with protein. The purest preparations of insulin are fairly stable and may be stored for 4 months without loss of potency; solutions may be heated at 80° for half an hour without marked destruction. Insulin does not diffuse readily through parchment membranes; it is adsorbed by charcoal from acid but not from neutral solution.

E. S.

Aqueous Extracts of Pancreas. III. Some Precipitation Reactions of Insulin. C. P. Kimball and J. R. Murlin (*J. Biol. Chem.*, 1923, 58, 337—346).—In developing a method for the preparation of insulin from aqueous extracts of pancreas a large number of both organic and inorganic precipitants have been tested, but the majority have been rejected owing to the difficulty of removing them from the precipitate. Among the more successful precipitants are amyl alcohol and sodium chloride. The former is used in conjunction with ethyl alcohol. Four to five volumes of ethyl alcohol are added to the aqueous extract; the addition of amyl alcohol then causes the insulin to separate as a solid layer between the aqueous and the alcoholic layers. Acetone also precipitates the insulin but it has the disadvantage that it precipitates at the same time a substance, to which the name *glucagon* is given, which produces a distinct hyperglycæmic effect in animals; it may be removed from the precipitated insulin by extraction with 95% alcohol. Saturation of an aqueous extract with sodium chloride causes complete precipitation of the insulin. Sodium chloride has the advantage over ammonium sulphate that traces of it are not harmful to the organism, whereas the ammonium sulphate, if not completely removed from the precipitate, may cause a hyperglycæmic reaction.

E. S.

Action of Ammonium Hydroxide and other Alkaline Compounds on Insulin. E. J. Witzemann and L. Livshis (*J. Biol. Chem.*, 1923, 58, 463—474).—Treatment of insulin with 0·5 or 0·7*N*-ammonia or with 0·1*N*-sodium or potassium hydroxide for some days causes complete inactivation. When ammonia has been employed, the activity may be quickly restored by acidification with hydrochloric acid; inactivation by sodium or potassium hydroxide, however, is irreversible. Sodium carbonate and hydrogen carbonate and disodium hydrogen phosphate have scarcely any action on the activity of insulin. When insulin is treated with mixed alkalis the inactivation may be either accelerated or retarded according to the mixture employed. The effect of ammonia is regarded as indicating a tautomeric change in the molecule.

E. S.

Chemical Reactions of the Substance containing Insulin. H. A. Shonle and J. H. Waldo (*J. Biol. Chem.*, 1924, 58, 731—736).—A detailed chemical examination of an insulin preparation from the pancreas of hogs. Precipitation and other methods of purification failed to separate a physiologically active substance of constant ultimate composition. The preparation appeared to be a complex mixture of proteoses, and the active principle itself may either be a proteose or be intimately associated with a proteose fraction.

G. M. B.

Adrenaline Secretion in Adrenaline Glycæmia. P. Trendelenburg (*Pflüger's Archiv*, 1923, **201**, 39—55; from *Chem. Zentr.*, 1924, i, 212).—Decomposition of glycogen results from the administration of smaller amounts of adrenaline than has been previously supposed. Blood-sugar in rabbits was increased by continuous administration of 0·00006—0·0001 mg. of adrenaline per kg. live weight per minute. Glycosuria does not appear unless larger doses are given. The secretion of adrenaline by the suprarenal bodies after the production of adrenaline hyperglycæmia was found to be more than 0·0005 mg. per kg. live weight per minute, a rate of production sufficient to cause glycosuria within a short time. There is probably a direct nervous stimulation of the liver cells in addition to the chemical effect. G. W. R.

Carbohydrate Metabolism of *Ascaris Megalocephala*. A. Fischer (*Biochem. Z.*, 1924, **144**, 224—228).—In view of the fact that the acid formation in autolysis of *Ascaris megalocephala* is accounted for by the breakdown of glycogen to lactic acid and carbon dioxide, doubt is expressed regarding the conclusions of Weinland (*Z. Biol.*, **42**, **43**), who regarded the acidity as being due to valeric acid, and the carbohydrate metabolism of these worms as being abnormal. J. P.

Fat Metabolism in Avitaminosis. V. Distribution of Fats and Lipoids in the Liver after Phosphorus Poisoning in Normal, Starving, and Avitaminosed Animals. K. Asada (*Biochem. Z.*, 1924, **144**, 203—211).—A histological study of the distribution of neutral fat in the livers of normal, starved, and avitaminosed rats confirms the author's earlier observations (A., 1924, i, 122, 245), but as regards lipoids, the microscopical appearance of the phosphorus-poisoned avitaminosed liver is the same as that of the poisoned normal liver despite the increased cholesterol content of the former as revealed by chemical methods. The conclusions of Salvioli and Sacchetto (*Frankf. Z. Path.*, 1922, **28**) regarding the effect of phosphorus poisoning on the fat and lipoid content of the livers of normal and starving dogs are based on too short periods of starvation. J. P.

Comparative Metabolism of certain Aromatic Acids. V. Fate of some Ring Substitution Products of Phenylacetic Acid in the Organisms of the Dog, Rabbit, and Man. L. R. Cerecedo and C. P. Sherwin (*J. Biol. Chem.*, 1923, **58**, 215—224).—When fed to human beings, dogs, or rabbits, *o*-nitrophenylacetic acid, *o*-aminophenylacetic acid, *o*-hydroxyphenylacetic acid, *o*-chlorophenylacetic acid, and 2 : 4-dinitrophenylacetic acid were excreted unchanged with the following exceptions: *o*-aminophenylacetic acid, which was excreted by rabbits in an acetylated form, and *o*-chlorophenylacetic acid, which was conjugated with glycine both in man and in the dog and excreted as *o*-chlorophenaceturic acid. All the above acids were less toxic than phenylacetic acid. The results show that *o*-compounds are not readily oxidised in the organism and that they are not necessarily more toxic than the *m*- and *p*-isomerides.

o-Chlorophenaceturic acid, m. p. 135°, has been synthesised from glycine and *o-chlorophenylacetyl chloride*, b. p. 119—121°/12 mm. The latter substance was obtained by the action of phosphorus pentachloride on *o*-chlorophenylacetic acid. E. S.

Detection of Pyruvic Acid in Muscle and Liver. L. J. SIMON and E. AUBEL (*Compt. rend.*, 1924, **178**, 657—659; cf. A., 1923, i, 875).—Pyruvic acid is not destroyed under aseptic conditions by macerated liver or fresh muscle. If injected as the sodium salt *in vivo* into the liver, it disappears, but not rapidly. Alanine, dextrose, and sodium lactate under similar conditions are not converted into detectable quantities of pyruvic acid. The latter, however, may possibly be produced in very small quantities, or undergo immediate conversion into other substances. E. E. T.

Specific Dynamic Action of Proteins. P. LIEBESNY (*Biochem. Z.*, 1924, **144**, 308—350).—The specific dynamic action of proteins, following the ingestion of 200 g. of flesh and 100 g. of bread, reveals itself in an increase of 20—40% above the oxygen consumption shown in the resting and fasting condition, the maximum increase occurring in from 1 to 2½ hours after the meal. For any one individual, the specific dynamic action is constant under like conditions over a period of some months. It is diminished or entirely lacking in cases of affection of the hypophysis and in conditions involving disturbance of the autonomic nervous system. Administration of preparations of the anterior lobe of the pituitary gland produces an increase in the specific dynamic action. J. P.

Adsorption of Amino-acids by Animal Tissues. W. MOELLER (*Biochem. Z.*, 1924, **144**, 152—158).—Hide powder adsorbs tyrosine from aqueous solution to the extent of 45% in 10 days. Importance is attached to the part played by such adsorption phenomena in the biosynthesis and hydrolysis of proteins. J. P.

Arginine Metabolism. K. FELIX and K. MORINAKA (*Z physiol. Chem.*, 1924, **132**, 152—166).—*dl*-Arginine, when passed through the liver of a cat, is hydrolysed fairly completely into ornithine and urea, both isomerides being attacked. Arginine, absorbed through the intestinal wall and then allowed to pass through the liver, is similarly hydrolysed by the liver. On the other hand, arginine in clupeon, which is built up of 2 mols. of arginine and 1 mol. of a monoamino-acid, is not hydrolysed by the liver. It would appear, therefore, that arginine, after absorption from the intestine, escapes complete destruction by the liver by being at least partly combined in the form of a polypeptide. W. O. K.

Animal Calorimetry. XXIII. Influence of the Metabolism of the Nucleic Acids on Heat Production. M. RINGER and D. RAPPORT (*J. Biol. Chem.*, 1923, **58**, 475—482).—It is concluded from experiments on dogs that nucleic acids exert no specific dynamic effect. E. S.

Metabolism of *l*-Pyrrolidonecarboxylic Acid and its Stability to Acids and Alkalis. R. M. BETHKE and H. STEENBOCK (*J. Biol. Chem.*, 1923, **58**, 105—115).—When fed in large amounts to pigs maintained on a starch diet, pyrrolidonecarboxylic acid is partly metabolised and partly excreted unchanged. No increase occurs in the amino-nitrogen content of the urine, thus indicating that the hydrolysis of the acid is not sufficiently rapid to lead to the production of glutamic acid in amounts greater than those which the organism can deaminise. The acidity and alkalinity of the alimentary canal are insufficient to account for the hydrolysis.
E. S.

Effects of Iodides on Nitrogen Metabolism. G. P. GRABFIELD, B. J. ALPERS, and A. M. PRENTISS (*J. Pharm. Exp. Ther.*, 1924, **22**, 393—400).—Administration of sodium or potassium iodides to man increases the output of nitrogen in the urine; the latter salt also increases the non-protein nitrogen of the blood.
W. O. K.

Effect of Reaction Changes on Human Inorganic Metabolism. J. B. S. HALDANE, V. B. WIGGLESWORTH, and C. E. WOODROW (*Proc. Roy. Soc.*, 1924, **B**, **96**, 1—14).—The alkalosis of forced breathing produces a fall in the inorganic phosphate of the blood accompanied by a fall in the excretion in the urine; the reverse effects are observed in the acidosis caused by the breathing of carbon dioxide. The ingestion of sodium bicarbonate produces no effect. In the acidosis following ingestion of ammonium chloride there is a heavy excretion of phosphate in the urine which falls off with the exhaustion of the available store of phosphate in the body, the immediate cause of the falling off being the low concentration of phosphate in the blood. Ammonium chloride acidosis also causes the body to lose large amounts of water, sodium, and potassium. C. R. H.

Acid–Base Metabolism. I. Determination of Base Balance. A. T. SHOHL and A. SATO (*J. Biol. Chem.*, 1923, **58**, 235—255).—Analyses have been made of the food, urine, and fæces of four male infants less than 1 year old. For purposes of calculating the acid–base balance, only sodium, potassium, calcium, magnesium, sulphates, phosphates, and chlorides are considered. Sulphur and phosphorus contained in the food are regarded as acidic constituents to the extent that they are oxidised in the organism to sulphates and phosphates. The results show that there is a normal positive base balance equivalent to 10 c.c. ± 2 c.c. of $0{\cdot}1N$ base per kg. per day. This balance is lowered by the addition of hydrochloric acid to the diet and raised by the addition of sodium hydrogen carbonate. The acid added to the food is excreted in the urine; the base, however, is excreted partly in the urine and partly in the fæces. E. S.

Acid–Base Metabolism. II. Mineral Metabolism. A. T. SHOHL and A. SATO (*J. Biol. Chem.*, 1923, **58**, 257—266).—Hydrochloric acid increases the excretion of ash, nitrogen, calcium, sodium, phosphorus, and chlorine in the urine of infants, and of ash, nitrogen, calcium, magnesium, and chlorine in the fæces, and decreases that of phosphorus in the fæces; the excretion of potassium, magnesium, and sulphur in the urine and of sodium and potassium in the fæces is unaffected. The net result is a decreased retention of ash, nitrogen, calcium, magnesium, sodium, potassium, phosphorus, sulphur, and chlorine. Sodium hydrogen carbonate increases the excretion of ash, nitrogen, sodium, potassium, sulphur, and chlorine in the urine, and of ash, nitrogen, calcium, sodium, potassium, phosphorus, sulphur, and chlorine in the fæces; it decreases the calcium, magnesium, and phosphorus in the urine, and the magnesium in the fæces. In this case, the net result is an increased retention of magnesium and sodium and a decreased retention of ash, nitrogen, calcium, potassium, phosphorus, sulphur, and chlorine. E. S.

Calcium Content of the Organs of Cats Treated with Calcium [Salts]. III and IV. H. Jungmann and M. Samter (*Biochem. Z.*, 1924, **144**, 265—269).—III. Determinations have been made of the distribution of calcium in the tissues of cats to which intravenous injections of calcium chloride and of calcium fructosephosphate had been given. After chloride administration the kidney showed a very high calcium content, and the lesser intestine, in contrast to that of normal animals, showed a uniform distribution of calcium along its entire length. Injection of calcium fructosephosphate, which has a more marked effect than has the chloride in increasing the calcium of the tissues generally, gave a notable increase in the calcium content of liver and kidney. IV. Intravenous injection of calcium chloride produces a greater increase in the calcium of the cat's kidney than does subcutaneous administration (cf. Heubner and Rona, A., 1923, i, 415). After intravenous injection of calcium fructosephosphate, the blood-serum and liver contain up to six times as much calcium as does the blood or liver of normal cats, or of cats given subcutaneous injections of calcium chloride. In acute calcium poisoning the calcium content of the skin may possibly be increased. Repeated injection of calcium acetate produces no alteration in the calcium content of the liver, heart, or other organs, nor does it affect the growth curves of the cats, as does subcutaneously administered calcium chloride (cf. Heubner and Rona, *loc. cit.*). J. P.

Metabolism of Inorganic Salts. IV. The Content of Inorganic Salts in the Blood in Pregnancy, with Especial Reference to Calcium. F. P. Underhill and Alice Dimick (*J. Biol. Chem.*, 1923, **58**, 133—140).—In general, little change occurs in the inorganic constituents of the blood during pregnancy, although the calcium content (determined on whole blood) is somewhat higher for pregnant than for non-pregnant women. The calcium content does not vary in a regular manner with the course of pregnancy. These results give no support to the view that an increased calcium content of the blood is of significance in the induction of labour. E. S.

Metabolism of Inorganic Salts. V. Inorganic Salt Metabolism in Cocaine Poisoning. F. P. UNDERHILL and E. G. GROSS (*J. Biol. Chem.*, 1923, **58**, 141—146).—No change is produced in the inorganic constituents of the blood by cocaine poisoning. The relief afforded by the administration of calcium salts is due to their action as central nervous depressants. E. S.

Absorption of Metallic Salts by Fish in their Natural Habitat. II. The Absorption of Nickel by *Fundulus Heteroclitus*. A. THOMAS (*J. Biol. Chem.*, 1924, **58**, 671—674; cf. *ibid.*, 1912, **11**, 381).—Nickel salts are not toxic to the *Funduli* in sea-water, but are extremely so in fresh-water, death being preceded by signs of intoxication in the fish. A number of analyses are given showing the dependence of the nickel absorbed on the concentration of the solution and on the time of immersion.

G. M. B.

Method of Determining the Biological Value of Protein. H. H. MITCHELL (*J. Biol. Chem.*, 1924, **58**, 873—903).—Details of the experimental methods are given, by which trustworthy data are secured on the nitrogenous metabolism of rats. The " metabolic nitrogen " of the fæces is measured by the total excretion of fæcal nitrogen on a nitrogen-free diet adjusted to have a " roughage " content approximately equal to that of the normal protein-containing diet. The excretion of nitrogen in the urine resulting from the catabolism of the tissues is not markedly depressed by protein feeding. The true basal catabolism of nitrogenous substances in the tissues is therefore measured by the total excretion of nitrogen in the urine in an adjacent period of feeding a nitrogen-free diet. This basal value is, however, subject to unexplained variations and must be redetermined at intervals in any long series of experiments.

The biological value of a protein is given by the percentage of the absorbed nitrogen (nitrogen intake — fæcal nitrogen of dietary origin) that is not eliminated in the urine. This value for the protein of a food is practically a coefficient of digestibility applied to the total protein present, and by means of it a " net protein value " of the food may be calculated. G. M. B.

Biological Value of Proteins at Different Levels of Intake. H. H. MITCHELL (*J. Biol. Chem.*, 1924, **58**, 905—922).—The biological values of the proteins (total nitrogen) of milk, maize, oats, rice, yeast, potatoes, navy beans, and the packing house by-product " tankage," have been determined by a modified Thomas method (preceding abstract). In the case of maize, milk, oats, and potatoes, experiments were made with rations containing 5 and 10% of protein, and, except for potatoes, the biological values were smaller at the higher level; the reasons for this are discussed. G. M. B.

Supplementary Relations among Proteins. H. H. MITCHELL (*J. Biol. Chem.*, 1924, **58**, 923—929).—If the biological value of the proteins in a mixture of two foods is found to be higher than that calculated from the values for each food used separately, assuming the effect to be directly additive, this shows the existence of a supplementary relation between the proteins of the two foods in question. A considerable supplementary relation has been shown to exist between the proteins of maize and of milk, and between those of maize and of "tankage.'" No such relation could be detected between gelatin and the proteins of the oat kernel. G. M. B.

Vitamins. I. Antineuritic Vitamins. G. Gaglio (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 479—482).—Many different substances are able to exert antineuritic properties, some of them removing all, and others only certain, of the symptoms of experimental polyneuritis in pigeons. Of all the materials which have been investigated, rabbits' urine produces the most complete and permanent antineuritic effects. Investigations are necessary to ascertain the action of different mixtures of the chemical compounds known to occur in urine or blood plasma when administered to pigeons in conjunction with polished rice. The known facts warrant the statement that the conception of a single specific antineuritic principle is not justifiable. T. H. P.

Presence of Vitamin-*A* in Commercial Lecithin. F. Eichholtz (*Biochem. Z.*, 1924, **144**, 70—71).—From feeding experiments on white mice the presence of vitamin-*A* in lecithin (Witte) is inferred. J. P.

Effect of Diet on the Content of Vitamin-*B* in the Liver. T. B. Osborne and L. B. Mendel (*J. Biol. Chem.*, 1923, **58**, 363—367).—When rats are maintained on a diet free from vitamin-*B*, the normal store of this factor in the liver is to a large extent depleted. E. S.

Fat-soluble Vitamins. XV. Calcium and Phosphorus Relations to Growth and Composition of Blood and Bone with Varying Vitamin Intake. R. M. Bethke, H. Steenbock, and M. T. Nelson (*J. Biol. Chem.*, 1923, **58**, 71—103).—Normal calcification takes place in the bones of rats maintained on a diet otherwise deficient in fat-soluble vitamins when 20 c.c. of skimmed milk or 1 c.c. of whole milk per rat per day is added to the diet; with smaller additions, the calcification is poor.

The femurs and humeri of normal rats yield 45% of ash at the age of 24 days, 59% at 66 days, and 66% at maturity. The blood phosphates and calcium are slightly higher in young than in old animals.

A quantitative relation appears to exist between vitamin and calcium whereby poor assimilation of the latter due to deficiency of the former in the diet may be counteracted by increases in the calcium content of the diet. When, owing to lack of vitamin or of calcium salts, normal growth does not occur, there is a tendency for the calcium content of the blood and the ash content of the bones to suffer a diminution. Absence of fat-soluble vitamins from the diet depresses the calcium content of the blood, the depression being increased by the addition of phosphates to the diet; radiation with ultra-violet light for 10 minutes per day increases both the calcium and phosphorus content of the blood. E. S.

Influence of Diet on Teeth and Bones. G. TOVERUD (*J. Biol. Chem.*, 1923, **58**, 583—600).—When guinea pigs are maintained on a diet deficient in antiscorbutic vitamin, both histological and chemical changes occur in the front teeth. The total ash and calcium content decrease whilst the magnesium content increases. White rats fed on a diet poor in calcium show a low calcium and a high magnesium retention and fail to breed normally. Their bones are low in total ash, calcium, and phosphorus, whilst the composition of their teeth is abnormal, the molars being low in total ash, slightly low in calcium and phosphorus, and slightly high in magnesium, and the front teeth low in all respects. Changes in the diet can thus produce chemical changes in a formed tooth. E. S.

Effect of Hæmatoporphyrin on the Deposition of Calcium in the Bones of Rachitic Rats. E. C. VAN LEERSUM (*J. Biol. Chem.*, 1924, **58**, 831—844).—Injection of hæmatoporphyrin causes a great increase in sensitiveness of the subject to rays of light lying within the visible part of the spectrum. The effect of such injections was therefore studied on rats in which, by a restricted diet, signs of rickets had been produced. *X*-Ray- and photomicrographs are given showing that under this treatment deposition of calcium was proceeding and the effects were similar to those of cod-liver oil or irradiation treatment. Direct proof of the influence of light has not yet been obtained. G. M. B.

Dietary Requirements for Reproduction. I. Nutritive Value of Milk Proteins from the Point of View of Reproduction. II. Existence of a Specific Vitamin for Reproduction. B. SURE (*J. Biol. Chem.*, 1924, **58**, 681—692, 693—709).—Rats fed on a complete artificial diet, with milk protein as a source of nitrogen, were found either to be sterile or to be unable to rear their young. Cod-liver oil was substituted for butter fat as a source of vitamin-*A*; vitamin-*B*, the antirachitic factor, and the necessary salts and iodine were provided. The further addition of casein, arachin, or edestin with 0·4% of cystine and in other experiments of lysine, proline, tyrosine, and trytophane still failed to secure normal reproduction. From these experiments and those of Evans and Bishop (*J. Metabol. Research*, 1922, **1**, 319, 335; 1923, **3**, 201, 233) it is concluded that there exists another hitherto unrecognised vitamin which is essential for reproduction. This factor has been found by breeding experiments to be present in Georgia velvet bean pod meal, polished rice, yellow corn, and rolled oats.

Accepting Macdonald's opinion that the "vitamin-*D*" of Funk and Dubin (A., 1922, i, 203) is wrongly classified as a vitamin, the term "*D*" is proposed for the antirachitic factor of McCollum and others (*J. Biol. Chem.*, 1922, **53**, 293), and the term "*E*" is adopted for the new vitamin which affects reproduction. G. M. B.

Chemical Changes in the Lipoids of Kidneys with Degenerated Cells. P. SCHNAPP (*Z. physiol. Chem.*, 1924, **133**, 62—79).—By clamping the vascular system of the kidney degeneration is induced in the cells of this organ. The ethereal extract of such degenerated kidneys showed a lower total lipoid content, a lower acidity (Spaltungzahl), and a lower iodine value than the normal kidney. On the other hand, the unsaponifiable and the saponifiable (Restzahl) residue showed an increase above the normal. S. S. Z.

R. Engeland and W. Biehler's Article "Some Compounds Extracted from Human Skeletal Muscle" (A., 1923, i, 72). J. A. SMORODINCEV (*Z. physiol. Chem.*, 1924, **132**, 328).—Attention is directed to the investigations by the author on the extractives of human and mammalian skeletal muscle (*Z. physiol. Chem.*, 1913, **87**, 12; 1914, **92**, 214; 1922, **123**, 116). J. P.

Saccharophosphatase in Human Organs. E. FORRAI (*Biochem. Z.*, 1924, **144**, 149—151; cf. A., 1922, i, 960; 1924, i, 120). —Saccharophosphatase is present in normal human pancreas and suprarenal bodies, but is absent from normal kidneys, testes, heart muscle, thyroids, skeletal muscle, and blood-serum. In cancerous conditions, it is found in certain organs (notably the liver) from which it is normally absent. J. P.

State of Combination of Nucleic Acids in Cell Nuclei. H. STEUDEL and T. TAKAHATA (*Z. physiol. Chem.*, 1924, **133**, 165—172).—The nucleic acid of yeast-cells is present in a free state and not in combination with protein. Nucleic acid was obtained from yeast by extraction with sodium chloride and precipitation with hydrochloric acid by Clarke and Schryver's method. S. S. Z.

Biological Significance of Nucleic Acid Compounds. E. HAMMARSTEN (*Biochem. Z.*, 1924, **144**, 383–465).—An important paper, in which the conductivity, hydrogen-ion concentration, osmotic pressure, and viscosity of thymus nucleic acid and its salts have been studied and discussed.

Thymonucleic acid is a strong polyphosphoric acid in which each of the four phosphorus atoms is associated with one dissociable hydrogen atom. Fresh thymonucleic acid dissolves to a concentration of about $3 \times 10^{-3}M$, yielding a turbid solution. It is supposed that the suspended particles causing the turbidity are due to the undissociated acid. From dialysis experiments carried out on the quadrivalent sodium salt of thymonucleic acid it is found that the salt possesses an apparent degree of dissociation of 0·25. The sodium salt of thymonucleic acid shows an osmotic pressure corresponding with that of the undissociated salt. On the other hand, when the acid is in combination with trimethyl-, triethyl-, or tripropyl-amine or with tetramethylammonium hydroxide, the osmotic pressure increases with the increase in volume of the cation. The sodium salt manifests the Donnan equilibrium in neutral solution. The relative viscosity of the sodium salt is very high, and it combines in dilute solutions with about 400 times its volume of water. Various agencies which lower the viscosity of its solution bring about an only partly reversible gel formation, which is most probably due to a phase reversal. The relative viscosity of the sodium salt is reduced by kations even in concentrations of less than $10^{-3}N$. The valency of the kations is of importance. Strong acids reduce the relative viscosity of sodium thymonucleate; the maximum reduction is reached when two of the sodium atoms are replaced by hydrogen. The viscosity of protein–nucleic acid salts is raised by the addition of sodium chloride, probably because of the formation of the tetrasodium salt by double decomposition. The ampholyte salts of thymonucleic acid are hydrolysed during dialysis if the ampholyte is diffusible. Salts of thymonucleic acid and proteins with an isoelectric point of p_H 4·7 exist as precipitates in equilibrium with the protein in hydrogen-ion concentrations approximating to the isoelectric point. When an excess of the sodium salt of thymonucleic acid is added, the protein salts dissolve in water at lower hydrogen-ion concentrations than $3—3{\cdot}5\times10^{-3}$. Protein and thymonucleic acid combine in varying proportions. Proteins with an isoelectric point of p_H 4·7 combine with thymonucleic acid during the first two stages of dissociation of the acid more readily than during the later stages of dissociation. Double decomposition takes place when the neutral salts of thymonucleic acid and diamino-acids are dialysed in the presence even of small quantities of sodium chloride with the formation of the sodium salt of the nucleic acid and the chloride of the diamino-acid. Histone compounds of thymonucleic acid are soluble in water when at least two of the sodium atoms of the salt and an equivalent of histone are in combination with 1 mol. of nucleic acid. The bearing of the above experimental observations on the biology of the cell is fully discussed, particularly with regard to the importance of the Donnan effect. S. S. Z.

Carbohydrate Group of Thymonucleic Acid. H. Steudel and E. Peiser.—(See i, 438.)

Distribution of Pentose Compounds in the Pancreatic Tissues of the Ling Cod (*Ophiodon Elongatus*, Girard). C. Berkeley (*J. Biol. Chem.*, 1923, **58**, 611—616).—Considerably more pentose is present in the islet than in the zymogenous tissue of the pancreas of the ling cod. It is suggested that it is produced from dextrose which has been activated by insulin.
E. S.

Nitrogenous Extractives from the Spleen. S. Demianowski (*Z. physiol. Chem.*, 1924, **132**, 109—133).—In spite of careful investigation of the phosphotungstic acid precipitate from the extract of the spleen of the freshly-killed ox, the presence of carnitine, methylguanidine, or of carnosine could not be detected. Tryptophan, approximately 0·0056% of the fresh horse spleen pulp, is extracted by water at 55—60°. Tryptophan is also extracted under similar conditions from the fresh spleens of oxen. Organic compounds other than tryptophan such as arginine, carnosine, tyrosine, or cystine are precipitated by Hopkins' reagent.
W. O. K.

Hydrogen-ion Concentrations within the Alimentary Tract of Insects. W. J. Crozier (*J. Gen. Physiol.*, 1924, **6**, 289—293).—Larvæ of dipterous insects (*Psychoda* and *Chironomus*) were kept in solutions containing an indicator (bromophenol blue, phenol red, or neutral red), and then removed and dissected. The colours of the fluid in the various sections of the intestinal canal indicated that the p_H was approximately as follows: in the œsophagus, 7·1; the cardiac chamber, 6·2; the mesenteron, 7·5; and the hind-gut, 6·4. W. O. K.

Behaviour of Calcium, Potassium, Chlorine, and Phosphorus in Milk and the Technique of Ultrafiltration. C. Wha (*Biochem. Z.*, 1924, **144**, 278—284).—Fifty % of the calcium of cow's milk is present in a colloidal non-diffusible form (cf. Rona and Michaelis, *ibid.*, 1909, **21**, 114), but in the process of souring all the calcium becomes ionised and diffusible. Of the phosphorus in milk 60% is in a colloidal state, whilst all the potassium and chlorine present is diffusible (cf. György, this vol., i, 120). A vacuum dialyser of collodion is described. J. P.

Influence of Phosphate and Bicarbonate on the Dissociation of Calcium Compounds in the Cerebro-spinal Fluid. H. Behrendt (*Biochem. Z.*, 1924, **144**, 72—80).—Using the method of Brinkman and van Dam, 20% of the total calcium (5 mg.%) of the cerebro-spinal fluid of children is found in the ionised condition at p_H 7·6—7·7. Sodium hydrogen carbonate and sodium hydrogen phosphate solutions of the same p_H as the fluid markedly lower the calcium-ion concentration, the phosphate exerting an effect more than twice that of the carbonate. J. P.

Ferments in the Amniotic Fluid. K. Maeda (*Biochem. Z.*, 1924, **144**, 1—8).—The reaction of the amniotic fluid varies between p_H 7·5 and 7·7. Diastase is present in the fluid in greater amount than in the blood from which it is derived. Lipase is sometimes present and originates from the fœtal intestine. Pepsin, rennin, and thrombin (fibrin ferment) occur only in traces. Trypsin is absent. J. P.

Urinary Excretion of Organic Acid and its Variation with Diet. L. McLaughlin and K. Blunt (*J. Biol. Chem.*, 1923, **58**, 267—284).—Determinations have been made by Van Slyke and Palmer's method (A., 1920, ii, 131) of the organic acid content of the urine of eight normal women. Under normal conditions, values (uncorrected for creatinine) equivalent to 6·8—10 c.c. of 0·1*N*-acid per kg. per day, which are similar to those obtained by Van Slyke and Palmer (A., 1920, i, 459) for men, were obtained. The amount excreted per hour by day (*i.e.*, during activity) was much greater than that by night. During fasting, the hourly excretion was equivalent to 15—24 c.c. of 0·1*N*-acid. This was markedly increased by diets rich in fruit or protein, but was only slightly affected by diets poor in these substances. One-third to one-half of the acids titrated by the above method consists of uric acid, creatinine, creatine, and amino-acids. Diets which increase the organic acid excretion also increase that of uric acid. E. S.

Creatinine Excretion of Women. L. McLaughlin and K. Blunt (*J. Biol. Chem.*, 1923, **58**, 285—290).—Determinations of the creatinine coefficients of eight normal women gave values (6·3—9·6 mg. of creatinine nitrogen per kg. per day) similar to those obtained by others for men. The higher values were obtained in the case of women who were below normal weight. There was no regular difference between the amounts excreted by day and those excreted by night. Creatine was almost invariably present in the day urine of one healthy woman. E. S.

Excretion of Ammonia and Nitrogen. R. S. Hubbard (*J. Biol. Chem.*, 1924, **58**, 711—719).—As the experiments of Marshall and Crane (A., 1923, i, 628) led to different conclusions from those drawn by Hubbard and Munford (A., 1923, i, 169) by a statistical examination of the results of analyses of human urine, a more extended series of figures has been obtained and examined as before. The results in general confirm the conclusions of Hubbard and Munford as to the excretion of ammonia by normal human subjects. G. M. B.

Effect of Injections of Sodium Phosphates and Sodium Hippurate upon the Excretion of Acid and Ammonia by the Kidney. B. M. Hendrix and J. P. Sanders (*J. Biol. Chem.*, 1923, **58**, 503—513).—Injections of disodium hydrogen phosphate or of sodium hippurate in fasting dogs cause an increase in the titratable acidity and in the ammonia content of the urine, the sum of these increases being practically equivalent to the salts injected. The results obtained support the view of Nash and Benedict (A., 1922, i, 191) that a portion of the urinary ammonia is formed in the kidney, but it is suggested that part may have its origin in the intestine. The kidney can probably retain sodium from sodium salts of acids as strong as hippuric acid, but is unable to do so in the case of much stronger acids. E. S.

Spontaneous Crystallisation of Uric Acid from Urine. L.-C. Maillard (*Bull. Soc. Chim. biol.*, 1923, **5**, 930—934).—It has been thought by some authors that uric acid is soluble in urine because it exists therein as a complex compound. The present author refers to an observation of his that uric acid crystallises spontaneously from urines which are markedly acid and show a high formol titration figure. He suggests that this may indicate that the compound mentioned above may be of the nature of an amino-acid complex. C. R. H.

Natural Porphyrins. V. Coproporphyrin in the Urine and Serum in Normal and Pathological Conditions. H. Fischer and W. Zerweck (*Z. physiol. Chem.*, 1924, **132**, 12—33).—Urine (1000 parts) is made acid with acetic acid (3 parts) and extracted with ether (1000 parts). The ether is washed with water (20 parts) and extracted with 25% hydrochloric acid (3 parts) and the solution observed spectroscopically. Coproporphyrin, if present, shows bands with centres at λλ *ca.* 592, 548, and 491. To the acid solution, ether, sodium acetate, and sodium hydroxide solution are added so that the mixture is still acid with acetic acid. The ethereal solution is then washed, and if coproporphyrin is present, it shows bands at λλ *ca.* 624, 567, 528. The coproporphyrin may be again extracted with acid and observed. Coproporphyrin has been found in the urine of normal individuals independently of whether their food has contained flesh or blood (cf. Schumm, A., 1923, i, 631, who found porphyrin present in normal subjects only after flesh or blood was consumed). From the united ethereal extracts, a solution containing cotporphyrin methyl ester, identified spectroscopically, was prepared. Coproporphyrin has been identified in the urine of guinea-pigs, in normal human serum, and in the serum of the horse, ox, and fowl. Investigations of the porphyrin in blood and urine in certain pathological conditions in man, as pernicious anæmia, hæmolytic icterus, and urobilinuria, are described. W. O. K.

Hæmatoporphyria Congenita. IV. The Identification of Natural Porphyrins in Serous Fluids and in Organs. O. SCHUMM (*Z. physiol. Chem.*, 1924, **132**, 62—71).—By means of spectroscopic observations, the presence of urinoporphyrin and of cotporphyrin has been detected in the pleural exudate from a patient suffering from hæmatoporphyria congenita. Details are given of the methods to be followed in examining such fluids or organs for the presence of porphyrins. W. O. K.

Hæmatoporphyrin of Human Fæces. A. PAPENDIECK (*Z. physiol. Chem.*, 1924, **133**, 97—99).—Polemical. S. S. Z.

Ether Extract of Fæces. A. D. HOLMES and R. H. KERR (*J. Biol. Chem.*, 1923, **58**, 377—381).—Experiments made in connexion with the digestibility of edible fats indicate that the amount of unutilised fat excreted in the fæces in the form of soaps is insignificant. Further, the ethereal extract of the fæces appears to be of a uniform composition independent of the particular fat ingested. E. S.

Decolorisation of Ethereal Extracts. J. MARKOFF (*Compt. rend. Soc. Biol.*, 1923, **89**, 113—115; from *Chem. Zentr.*, 1924, i, 80).—Directions are given for the use of phosphotungstic acid for decolorising ethereal extract of fæces. Preliminary removal of the ether by distillation is necessary. G. W. R.

Adsorption and the Distribution of Drugs in the Organism. III. E. KEESER (*Biochem. Z.*, 1924, **144**, 536—544).—There is no parallelism between the adsorption capacity of charcoal for alkaloids and iodine *in vitro* and its detoxicating effect in the intestinal tract of the dog. The method by which a charcoal is prepared and not its origin is the determining factor of its adsorptive capacity. Strychnine nitrate is adsorbed more readily than morphine hydrochloride. In the presence of sodium bicarbonate, morphine hydrochloride and strychnine nitrate are adsorbed to a higher extent by charcoal. The electric charge changes in blood charcoal (Kahlbaum) at p_H 3·5, in beech charcoal (Kahlbaum) at p_H 6·6, in "carbovent" at p_H 3·9. There is no change in the electric charge in bone charcoal (Kahlbaum), beech charcoal (Merck), and lime tree charcoal (Kahlbaum) at the investigated range of hydrogen-ion concentration. S. S. Z.

Action of Different Substances, particularly the so-called Heart Remedies, on Disturbances of the Rhythm of the Heart. W. SIMON (*Arch. Pharm. Exp. Ther.*, 1924, **100**, 307—315).—Only caffeine, calcium salts, human serum, and especially adrenaline, out of a large number of substances investigated, were able to relieve the disturbance of the rhythm of an isolated frog's heart, caused by cocaine or strychnine. W. O. K.

Physico-chemical Technique for Detection of Polonium injected into Organs. (MME.) J. S. LATTÈS and A. LACASSAGNE (*Compt. rend.*, 1924, **178**, 630—632; cf. this vol., i, 347).—The organ into which polonium has been injected is treated with potassium chlorate and hydrochloric acid until destroyed (fats, unaffected by this reagent, may then be separated mechanically); the solution obtained is boiled in presence of silver foil, and the polonium deposited on the latter determined by measuring its activity. This method is much more sensitive than the auto-histo-radiographic method, but obviously gives only the mean polonium content of an organ and not the distribution of that element. E. E. T.

Influence of "Alkaloids" on Permeability. W. HEUBNER (*Biochem. Z.*, 1924, **144**, 351—352).—The suggestion is made that the observations of Brinkmann and Szent-György (A., 1923, i, 974) on the action of morphine and codeine salts on the permeability of a collodion membrane to hæmoglobin, may have had their origin in the action of the anion; the work of Rhode (A., 1922, i, 1088) on the action of morphine chloride and codeine phosphate on hæmolysis is cited in this connexion. J. P.

Vasodilatation by Amino-acids in Isolated Dog Kidneys. H. FREDERICQ and L. BROUHA (*Compt. rend. Soc. Biol.*, 1923, **89**, 665—667; from *Chem. Zentr.*, 1924, i, 213).—Glycine, *l*-leucine, *d*-alanine, and *dl*-valine exert a vasodilatory effect in isolated dog kidneys, which is demonstrated by the increased flow of liquid from the renal vein and the ureter. The action of *dl*-phenylalanine is less definite. G. W. R.

Effect of Amino-acids on Exchanges in Isolated Organs. H. FREDERICQ and L. MÉLON (*Compt. rend. Soc. Biol.*, 1923, **89**, 668—669; from *Chem. Zentr.*, 1924, i, 213; cf. preceding abstract).—Isolated dog kidneys were perfused with Locke solutions containing 0·5% of different amino-acids. The first result was the production of an acid reaction, an effect not observed with Locke solution alone. *d*-Alanine and *l*-leucine cause an increase in nitrogen titratable by formaldehyde in the liquid. Other compounds have no effect or depress the amount of nitrogen titratable by formaldehyde. G. W. R.

Detection of Toluene in Organs and its Distribution in the Organism. S. Kuroda (*Biochem. Z.*, 1924, **144**, 287—293).—The toluene is distilled from a suspension of the organ in water and collected in carbon tetrachloride. It is nitrated, dissolved in water, made alkaline with sodium hydroxide, extracted with ether, and finally weighed. After toluene poisoning, the central nervous system of dogs and guinea pigs contains more toluene than the other organs, with the exception of the spleen, and the leucocytes of the blood are diminished. J. P.

Effect of Chloroform and Phosphorus Poisoning on Carbohydrate Tolerance. M. Bodansky (*J. Biol. Chem.*, 1923, **58**, 515—522).—Experiments on dogs indicate that the lævulose tolerance test described in this paper is of great value in measuring the degree of liver injury during chloroform and phosphorus poisoning. Dextrose and galactose are not suitable for this purpose. E. S.

Action of Hydrazine and some of its Derivatives in producing Liver Injury as measured by the Effect on Lævulose Tolerance. M. Bodansky (*J. Biol. Chem.*, 1924, **58**, 799—811).—The degree of liver injury produced in dogs by hydrazine and a number of derivatives have been determined by the lævulose tolerance test previously described (cf. preceding abstract), and the results confirmed by *post-mortem* examination. Hydrazine, phenylhydrazine, *s*-di*iso*propylhydrazine, and ββ-azopropane ($CHMe_2{\cdot}N{:}N{\cdot}CHMe_2$) are highly injurious to the liver, whereas methylphenylhydrazine, diphenylhydrazine, acetylphenylhydrazine, and *p*-hydrazinobenzoic acid have much less effect. G. M. B.

Influence of Hydrazine on Blood Concentration and Blood-sugar Content. F. P. Underhill and S. Karelitz, jun. (*J. Biol. Chem.*, 1923, **58**, 147—151).—The hypoglycæmia produced in dogs by the subcutaneous injection of hydrazine hydrate (cf. A., 1914, i, 632; 1915, i, 1037) is preceded by a transitory condition of hyperglycæmia; no sugar, however, appears in the urine. Hydrazine poisoning also causes a marked increase in blood concentration, which is ascribed both to the loss of fluid and to the inability of the animal to retain food or water; this effect probably contributes largely to the fatal results. There is no direct relationship between the degree of blood concentration and the extent of hypoglycæmia. E. S.

Specificity of the Intracellular Hydrogenases in Frog's Muscle. M. E. Collett (*J. Biol. Chem.*, 1924, **58**, 793—797).—The influence of certain protoplasmic poisons on the oxidation of citric and succinic acids by washed frog's muscle in presence of methylene-blue has been examined. The action is more readily inhibited by phenol and chloral hydrate in the case of the oxidation

of citric acid than in that of succinic acid: this order is reversed with poisons such as tellurites, selenites, selenates, and arsenates. The conclusion is drawn that there are two enzymes specific for the oxidation of citric and succinic acids, respectively.
G. M. B.

Fungal Product, $C_6H_6O_4$, and its Behaviour on Hydration. N. WIJKMAN (*Z. physiol. Chem.*, 1924, **132**, 104—108).—When *Aspergillus* spp. are grown on a medium containing sucrose in quartz or paraffined glass flasks and the acidity of the medium is kept within certain limits, there regularly separate from the culture liquid crystals of a *substance*, which after sublimation under a low pressure melts at 154° and possess the formula $C_6H_6O_4$ [*copper* salt, $(C_6H_5O_4)_2Cu,H_2O$; *acetyl* compound, $C_6H_4O_2(OAc)_2$]. On treatment with hydrogen in presence of a catalyst, a compound, m. p. 80—90°, b. p. *ca.* 200°/1 mm., is obtained, which appears to be hydroglucal, although this has not been proved conclusively.
W. O. K.

Simultaneity of Two Contradictory Toxic Effects (Immunity and Anaphylaxis) on the Same Cell. C. RICHET, (MLLE.) E. BACHRACH, and H. CARDOT (*Compt. rend.*, 1924, **178**, 535—537).—The lactic acid bacillus, if cultivated in presence of copper sulphate (or of mercuric chloride) and potassium arsenate together, acquires simultaneously sensitivity towards the former and immunity towards the latter. E. E. T.

Diphtheria Toxin and Anatoxin. Flocculating Power and Immunising Properties. G. RAMON (*Ann. Inst. Pasteur*, 1924, **38**, 1—10).—Antidiphtheria serum produces a flocculation when added to diphtheria toxin. The amount of antitoxin required to cause flocculation measures the toxicity of the toxin. When diphtheria toxin, to which formalin (3 or 4 parts per 1000) had been added to prevent bacterial contamination, was kept at 40—42°, it lost its toxicity, but retained its property of being flocculated by antitoxin. The *anatoxin* so produced retains also the immunising power, *in vivo*, of the original toxin, and its strength may be estimated by finding the amount of antitoxin required to cause flocculation, as this has been found experimentally to be proportional to its immunising effect. W. O. K.

Antiseptic Value of Hexamethylenetetramine *in vitro*. A. DUTHOIT (*Compt. rend. Soc. Biol.*, 1923, **89**, 656—658; from *Chem. Zentr.*, 1924, i, 71).—With 2% hexamethylenetetramine in Ringer solution, paratyphoid and typhoid bacilli are completely killed in 4—7 days. *Bacillus coli* and pneumobacilli are not completely killed, even after 10 days. The antiseptic effect of hexamethylenetetramine does not reside in the formaldehyde group.
G. W. R.

Antiseptic Effect of Hexamethylenetetramine. A. DUTHOIT (*Compt. rend. Soc. Biol.*, 1923, **89**, 658—660; from *Chem. Zentr.*, 1924, i, 71; cf. preceding abstract).—Data are given for the bactericidal effect of the gall of dogs on different species of bacteria with and without preliminary injection of hexamethylenetetramine. It is found that hexamethylenetetramine is less effective as an antiseptic *in vivo* than *in vitro*. G. W. R.

Effects of Electrolysis on Animal Tissue Enzymes. Abundance of Silicic Acid in the Ash. F. MAIGNON (*Compt. rend.*, 1924, **178**, 654—657).—The enzymes from all body-tissues examined contained silica and calcium. Some tissue enzymes also contained characteristic quantities of phosphorus, arsenic, magnesium, and iron. Electrolysis of the enzyme preparations in aqueous solutions gave a coagulum at both anode and cathode with concomitant loss of therapeutic properties (cf. this vol., i, 350). E. E. T.

Rapid Analysis of Sugars. Purification and Concentration of Enzyme Solutions. F. W. REYNOLDS (*Ind. Eng. Chem.*, 1924, **16**, 169—172).—Yeast extracts may be freed from colour and substances causing turbidity by dialysing or by washing on an ultra-filter and subsequently acidifying with acetic acid, whereby the substances causing turbidity are flocculated and can be removed by filtration through paper. Highly active preparations of invertase and melibiase may be obtained by concentrating crude or purified yeast extracts by ultra-filtration. A simple ultra-filter with a collodion membrane is described and illustrated. The impurities, especially those which are optically active, are largely eliminated and not concentrated with the enzyme. The activity of enzymes prepared by these means was about eight times that of the ordinary yeast extracts, and was such that sucrose solutions could be completely hydrolysed with their aid in 15 minutes at the ordinary temperature. Ultra-filtration should be useful as a means of concentrating other enzymes for use as analytical reagents and also in the study of the enzyme action of plant and fruit juices. H. C. R.

Purification of Toxins, Ferments, and other active Biological Organic Colloids. L. MICHAELIS and H. DAVIDSOHN (*Biochem. Z.*, 1924, **144**, 294—297).—Details are given of the patented process (1912) used for purifying toxins, ferments, etc., by precipitation at the isoelectric point or at a definite hydrogen-ion concentration. J. P.

Mechanism of Alcoholic Fermentation. III. A. LEBEDEV (*Z. physiol. Chem.*, 1924, **132**, 275—296).—Yeast incubated with sucrose in the presence of sodium sulphite and sodium or potassium dihydrogen phosphate, yields compounds the osazones of which (m. p. 202—209°) are free from phosphorus, but in the presence of these phosphates alone the osazones obtained (m. p. 143—152°) are those of phosphate esters differing from hexose biphosphate, whilst the presence of disodium or dipotassium hydrogen phosphates may or may not lead to the formation of a phosphate ester, the results varying with different yeast preparations. Whilst the analyses of the various phosphate esters has not yet been completed, it is apparent that it is possible to control, not only the amount, but also the nature of the hexose phosphate formed during yeast fermentation. The author supposes yeast fermentation to proceed in acid solution as follows: hexose ⟶ two trioses ⟶ glyceric acid ⟶ pyruvic acid ⟶ acetaldehyde ⟶ alcohol ⟶ carbon dioxide, whilst in neutral or alkaline solutions glycerol is formed along with glyceric acid and acetic acid accompanies alcohol. The formation of the four known hexose phosphates (including the new osazone-forming monophosphate described by the author) is correlated with the preliminary formation of glyceraldehyde, dihydroxyacetone, and the two corresponding monophosphates of these compounds. In accord with the author's views the presence of nine individual enzymes in the zymase complex is postulated. J. P.

Influence of Amines on Fermentation. II. J. ORIENT (*Biochem. Z.*, 1924, **144**, 353—360).—The effect of various alkylamines and their salts, glucosamine and its hydrochloride, diamines, and indole derivatives on yeast fermentation has been investigated. In general the salts of amines and diamines increase, whilst the free bases diminish fermentation. Indole has a slight inhibiting action, whilst scatole has the reverse effect (cf. A., 1923, i, 171). J. P.

Action of Drugs containing Hydroxymethylanthraquinones on Fermentation. J. ORIENT (*Biochem. Z.*, 1924, **144**, 361—365).—The action of various pharmacological preparations of *Rheum*, *Aloe*, *Senna*, *Cascara*, *Frangula*, *Cassia*, *Jalappa*, and *Colocynthis* on yeast fermentation has been investigated. In general fermentative action is increased, more especially by the rhubarb group rich in hydroxytrimethylanthraquinone. J. P.

Fermentation with Non-ferments. W. BIEDERMANN (*Z. angew. Chem.*, 1924, **37**, 71—73).—If a solution containing diastase (*e.g.*, saliva or a solution of saliva albumose) is heated, a turbidity appears at 70—80°, owing to partial coagulation of the "zymogen," and the diastatic power is considerably diminished; it does not, however, disappear even by heating the solution to boiling, and may be considerable in the presence of oxygen. This regeneration by means of air is further enhanced by the presence of the above coagulate. A solution of saliva ash, or even simple salt solutions (particularly sodium chloride), can produce a slow degradation of amylose to sugar, although here again thorough aëration is necessary. The activity of the salts is increased, not only by the specific protein, but also by the inactive degradation products, the presence of amino-acids (*e.g.*, glycine, leucine) being found advantageous. It appears that the organic ferment, and not the inorganic substance, should be regarded as the activator. Treatment of fibrin with steam yields solutions which, after addition of sodium chloride or a suitable phosphate mixture, are capable of fermenting amylose, if an adequate supply of air is maintained. By employing very dilute ferment solutions amylose can be converted into dextrin alone, without a simultaneous production of sugar. It may, finally, be said that, below a certain dilution, small quantities of saliva diastase have exactly the same action as the "complementary" inorganic salts alone, provided the latter are in a corresponding concentration. W. T. K. B.

Comparison of the Action of Acids and Enzymes in Hydrolytic Phenomena. H. COLIN and A. CHAUDUN (*J. Chim. physique*, 1923, **20**, 471—483).—The hydrolysis of sucrose by diastase is considered theoretically and it is shown that the velocity of the reaction does not increase with the concentration of the sucrose (a) nor with the concentration of the diastase (n), but rather with the ratio of these concentrations, a/n. The condition under which the reaction follows Wilhelmy's law is that a/n shall be less than a value a'/n' which is characteristic of the solution of diastase employed. When $a/n<a'/n'$ then the amount of sucrose transformed each instant can be calculated by Wilhelmy's formula $x=a(1-e^{-kt})$, which means that under these conditions the rates of hydrolysis by acids and diastase are identical. When $a/n>a'/n'$ the initial velocity $v=f(an)$ is independent of a and proportional to n. These facts indicate that the enzyme forms a complex with the sugar, which then decomposes with a finite velocity in keeping with the law of mass action. The above statements apply exactly to the action of emulsin on glycosides. The velocity of inversion by diastase decreases with increasing viscosity of the solution, but in the case of hydrolysis with acids the viscosity appears to have no influence on the velocity of the change. J. F. S.

Inactivation of Invertase in Fresh Yeast by Silver Nitrate. H. VON EULER and E. WALLES (*Z. physiol. Chem.*, 1924, **132**, 167—180).—The invertase of yeast-cells is inactivated by silver nitrate as the latter is taken up from the solution by the cells. It may regain its activity by self-regenerative processes or by treatment with hydrogen sulphide. The phenomenon is therefore parallel to the inactivation of yeast enzymes in solution (Euler and Myrbäck, A., 1922, i, 959). Yeast inactivated by silver nitrate and regenerated by treatment with hydrogen sulphide shows, after incubation, an increased activity. Owing to these protective mechanisms the invertase of the living yeast-cell is two hundred times more resistant to the toxic action of silver than is the same amount of the enzyme in solution. Zymase is much more susceptible to inactivation by silver than is invertase. J. P.

Invertase. III. H. VON EULER and K. JOSEPHSON (*Ber.*, 1924, **57**, [*B*], 299—302; cf. A., 1923, i, 721).—The maximum purification of invertase preparations by the author's methods appears to be reached when the value If^0 attains about 250.

Determinations of the molecular weight of invertase by measurements of diffusion indicate that the "active group" is contained in or associated with a complex of molecular weight about 20,000.

Specimens of invertase have been obtained in which the ash does not exceed 0·13%; the higher ash content of previous preparations is therefore due to impurities. The acidic and basic dissociation constants have been determined provisionally to be $K_a=10^{-7}$ and $K_b=10^{-11}$, respectively. The isoelectric point of invertase at 20° is calculated to be at p_H 5. H. W.

Affinity of Invertase for Different Sugars. H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **132**, 301—327).—At p_H 4·5 invertase of bottom yeasts has a marked affinity for both α- and β-dextrose, the affinity being slightly greater in the latter case than in the former. The affinity for lævulose is of the same order as for dextrose. In contrast to the findings of Kuhn (*Z. physiol. Chem.*, 1923, **127**, 234; **129**, 57), no general support is forthcoming for the view that separate "gluco-" and "fructo-" invertases exists. The affinity of invertase for other hexoses and pentoses depends on the presence of a free reducing group (aldehydic or ketonic) and on the configuration of the remainder of the molecule, which may be considerably modified without entirely abolishing the affinity. In general, the β-forms of the hexoses and pentoses show a greater affinity than the α-forms except in the cases of dextrose and xylose, where both stereoisomerides react practically alike. A relation appears to exist between the configuration of the sugar molecule and the relative affinity of invertase for its α- and β-forms; thus the pairs dextrose–xylose and galactose–arabinose give parallel results. The affinity of invertase for the disaccharides has also been studied but no very definite conclusions are drawn. J. P.

Uniformity in Invertase Action. J. M. NELSON and F. HOLLANDER (*J. Biol. Chem.*, 1923, **58**, 291—304).—The abnormality observed with certain invertase preparations (A., 1922, i, 388) has been shown to be due to inactivation. Thus, when the abnormal preparations were incubated at 25° with a citrate buffer mixture at p_H 4·5 (the acidity at which the abnormality was observed) some loss of activity occurred, whilst this was not the case with normal preparations. Further, addition of sodium chloride or of boiled normal invertase prevented inactivation in the case of the preparation which was rendered normal by this treatment, but did not do so with the second abnormal preparation, which could not be rendered normal in this way. At 25° the point of maximum stability of one abnormal and two normal invertase preparations was found to lie, not at the acidity for maximum activity (p_H 4·5; cf. Euler and Laurin, A., 1920, i, 506), but on the alkaline side of this (about p_H 5·8). E. S.

Enzyme Adsorption. I. H. KRAUT and E. WENZEL. A Contribution to the Knowledge of "Invertin" of Willstätter and his Collaborators (*Z. physiol. Chem.*, 1924, **133**, 1—21).—The adsorption curve obtained by adsorbing the invertase of autolysed yeast juice with aluminium hydroxide deviates from the normal adsorption isotherm. The author argues that this is due to the interference of impurities adsorbed from the juice. Any change in the initial activity of an impure juice yields a different adsorption curve. In certain cases, it is even possible for aluminium hydroxide to adsorb more of the enzyme out of dilute impure solutions than out of similar solutions of higher concentration. The adsorption value rises with the purity of an invertase preparation. S. S. Z.

Influence of Alkaloids of the Atropine, Cocaine, and Morphine Groups on Yeast Invertase. P. RONA, C. VAN EWEYK, and M. TENNENBAUM (*Biochem. Z.*, 1924, **144**, 490—519).—A series of alkaloids of the above groups have been found to possess an inhibiting influence on the action of yeast invertase. Although the intensity of the inhibition varies with the various alkaloids, the general inactivating influence proceeds logarithmically according to the concentration of the alkaloid present. The inhibition is reversible, and is influenced by the hydrogen-ion concentration of the medium. No connexion exists between the optical configuration and the inhibitory power of *dl*-atropine and *l*-hyoscyamine; *l*-cocaine and *dψ*-cocaine; and *l*-ecgonine and *d*-ecgonine. In none of these three cases was there any difference between the inhibitory power of the isomers. Tropine inhibits much less markedly than atropine, whilst tropic acid does not inhibit at all; nor does an equimolecular mixture of tropine and tropic acid have a greater inhibiting effect than tropine alone. *d*- and *l*-Ecgonine do not inhibit, but, on the other hand, the chemically-related cocaine does. The substitution of the hydrogen of morphine by the methyl group (codeine) produced no apparent change in inhibitory power, but substitution by ethoxyl (dionine) produced a small though definite change. S. S. Z.

Heat and Radiation Inactivation of Malt Amylase. H. LÜERS and P. LORINSER (*Biochem. Z.*, 1924, **144**, 212—218).—The zone of maximal thermostability of malt amylase is displaced towards higher p_H values by increased concentration of an acetate buffer. Gelatin, egg-albumin, and gum arabic protect the amylase from heat inactivation especially between p_H 6·0 and 7·0, and produce a flattening of the zone of maximum stability. Maltose has a similar protective influence and a direct proportionality exists between log $C_{maltose}$ and the coefficient of inactivation. The inactivation of amylase by ultra-violet radiation follows neither the mono- or bi-molecular equation, nor the Schütz law. The effect of alterations in the hydrogen-ion concentration is much less marked in this case than in that of heat-inactivation. The temperature coefficient for ultra-violet inactivation is k^{30}/k^{20} 1·30, and physicochemically the two methods of inactivation are dissimilar. J. P.

Ferments and Light. IV. Diastase. III. L. PINCUSSEN and F. DI RENZO (*Biochem. Z.*, 1924, **144**, 366—371; cf. A., 1924, i, 107).—The inactivation by ultra-violet light of 0·1% of malt diastase acting on 1% starch solution at varying p_H proceeds as a unimolecular reaction, whilst in the presence of 0·5% of starch only the later stages correspond with the unimolecular equation. The departure from the simple equation is still more marked in the presence of 0·25% of starch. A 0·2% solution of the enzyme gives complex results in the presence of 1·0, 0·5, and 0·25% starch solutions. J. P.

Ferments and Light. V. Diastase. IV. L. Pincussen (*Biochem. Z.*, 1924, **144**, 372—378).—Sodium chloride protects both the diastase and maltase in malt diastase from inactivation by exposure to sunlight. $M/6$-Phosphate solution protects malt diastase and the maltase of " pancreatin Rhenania " from inactivation by ultra-violet light, whilst more dilute phosphate solutions are less effective. Similar results are given by acetate solutions of the same p_H. In the presence of a phosphate buffer, with or without the addition of sodium chloride, the protective action is at a maximum at p_H 6·64. Ammonium, potassium, and lithium chlorides, potassium bromide, and sodium fluoride protect taka-diastase from ultra-violet light to varying degrees, an effect which is more marked in dilute solutions of these salts than in more concentrated solutions. Potassium and sodium nitrates and nitrites give similar results but do not show the same varying effects at different temperatures. J. P.

Purification of Ferments by Electro-dialysis and Electro-Osmosis. I. Malt Diastase. R. Fricke and P. Kaja (*Ber.*, 1924, **57**, [*B*], 310—313).—Electro-dialysis of solutions of malt diastase is effected in a cell divided into three compartments by collodion membranes. The central compartment contains the solution of malt diastase, whilst the outer compartments contain distilled water and the iron gauze cathode and carbon anode, respectively. The voltage used is 220 or 22. As soon as the current has attained a strength of 0·0045—0·006 amp. per sq. cm. the solution in the outer cells is replaced by distilled water and the process is repeated until the current strength remains practically constant at its initial value after recharging the anode and cathode cells. The dry matter concentration of the solution of malt diastase is very considerably lowered, whilst the activity of the enzyme towards starch is increased 2·1 to 2·5 times. After concentration by cautious freezing, the diastase solution gives slight protein but marked carbohydrate reactions. The ash is diminished from 5% to 1%, the nitrogen content from 6·14% to 3·51%.

Electro-osmosis is conducted in a five-compartment cell in which the extreme compartments which contain the electrodes are separated from the intermediate compartments by collodion membranes impermeable to diastase. The barrier between the intermediate and central cells is of collodion permeable to diastase. The central compartment contains the malt diastase solution, the others contain water. The pressure used is 22 volts. After electro-osmosis during 5 days, 39% of the malt diastase remains in the central compartment and shows a diminution in activity from 2·4 to 0·8, 32% has passed towards the anode and is inactive towards starch, 16% has passed towards the cathode and has increased in activity from 2·4 to 4·6, whilst 13% remains in the membranes. The highly active malt diastase gives a marked positive reaction for carbohydrates; it contains carbon 56·4%, hydrogen 7·9%, and nitrogen 3·28%. H. W.

Non-homogeneity and other Properties of Malt Diastase. R. Fricke and P. Kaja (*Ber.*, 1924, **57**, [*B*], 313—316).—A comparison of the starch-liquefying and saccharifying powers of Merck's "diastase absolut" with those of preparations purified by the authors' methods (preceding abstract) shows these properties to be affected to the same degree with respect to soluble starch; the purified product, however, appears to be relatively deficient in starch-liquefying power towards potato starch, thus supporting von Euler's hypothesis ("Chemie der Enzyme," II, 1922, 116) that at least two components are present in malt diastase. The previous conclusion that the presence of proteins in crude malt diastase is not essential to its diastatic properties is strengthened by the observation that the ferment is not affected by prolonged treatment with trypsin. Uranyl acetate is harmless as long as proteins are present with which it forms a precipitate, but after this point is passed, it acts as a vigorous poison. H. W.

Amylolytic and Glycolytic Enzymes of the Pancreas and the Salivary Glands. C. Serono and A. Cruto (*Rass. Clin. Terap. Sci. aff.*, 1923, **22**, 139—142; from *Chem. Zentr.*, 1924, i, 62).—A glycerol extract of pancreas, an aqueous extract of dried sterilised pancreas powder, or salivary diastase, does not form maltose or dextrose from starch solution, but only *iso*maltose. The amount of *iso*maltose formed depends on the concentration of starch. The amylolytic enzyme from pancreas, after separation from lipolytic and proteolytic enzymes, is unstable, but can be stabilised by the addition of plant colloids to the solution. The presence of colloidal material increases the stability to heat of the pancreatic and salivary enzymes. The glycolytic enzyme obtained from the pancreas (Serono and Cruto, *Arch. Farm. Sperim.*, 1913, **14**, 501) is held to be an inner enzyme liberated by maceration, and may be obtained from other tissues in the same way. Only small quantities of ethyl alcohol and carbon dioxide are obtained by its action. It is concluded that no enzyme capable of synthesising sugar occurs in the pancreas. Glycogen is probably formed from *iso*maltose and not from the polymerisation of dextrose. Liver glycogen is only slightly attacked by pancreatic extract under aseptic conditions. G. W. R.

Presence of Inulase in Takadiastase. Y. Takahashi (*Biochem. Z.*, 1924, **144**, 199—202).—Takadiastase contains an inulase capable of hydrolysing inulin to lævulose. J. P.

Inulin and Inulase. IV. H. Pringsheim and G. Kohn (*Z. physiol. Chem.*, 1924, **133**, 80—96).—When inulin is heated in glycerol it is "dissociated" into polymers which consist of 8—10 monoses. Such "dissociated" inulin gradually acquires the properties of "associated" inulin when in solution and eventually separates out as such. The most favourable reaction for the action of inulase on inulin is p_H 3·8, and the hydrolysis proceeds according to the formula of a unimolecular reaction.

Press juices of inulase obtained from older moulds (*Aspergillus niger*) were more active than those derived from younger moulds. The reaction constants have been worked out for inulins of various degrees of purity and for "dissociated" inulin (obtained by heating inulin in glycerol). Invertase hydrolyses inulin and "dissociated" inulin at a hydrogen-ion concentration of the order of that of gastric juice. *Aspergillus niger* contains an invertase as well as an inulase. S. S. Z.

Polysaccharides. XXII. Lichenase and Reserve Cellulose (Lichenin). P. KARRER, M. STAUB, A. WEINHAGEN, and B. JOOS (*Helv. Chim. Acta*, 1924, 7, 144—154).—Lichenin, which has already been recognised as a form of cellulose (A., 1923, i, 1182), is now identified with so-called reserve cellulose. It follows that the enzyme lichenase is closely related to cytase. Since the latter, however, contains enzymes which attack not only reserve celluloses but mannan and galactan, the term lichenase is retained for the enzyme obtained from the snail, *Helix pomatia*. The crude snail extract contains, besides lichenase, a variety of other enzymes, including invertase, lipase, diastase, inulase, maltase, and a cellobiase. The lichenase can be purified from the accompanying enzymes by dialysing, since all of them, with the exception of cellobiase, are unstable in water and quickly disappear. Some of the lichenase is lost during the purification, since it can diffuse through a membrane. The lichenase is best isolated by precipitation from the dialysed solution with acetone. The enzyme rapidly loses its activity if heated above 36°. The most active lichenase preparations are those which have not passed through a drying stage. Basic aluminium sulphate adsorbs lichenase almost completely from neutral solution; the enzyme can be brought into solution again by potassium dihydrogen phosphate and the solution so obtained can be purified by dialysis. Aluminium hydroxide also adsorbs the enzyme completely, but recovery is not so good as from the basic sulphate. The activity of lichenase solutions is not affected by sodium chloride, albumin, or soap, but is lowered by all sugars. The work of Pringsheim and Seifert (A., 1923, i, 998) indicates the presence of lichenase in barley, and it appears to be present in many other plants. Plant lichenase is, however, difficult to separate from accompanying enzymes. E. H. R.

Polysaccharides. XXIII. Separation of Lichenase into Constituent Enzymes. P. KARRER, M. STAUB, and B. JOOS (*Helv. Chim. Acta*, 1924, 7, 154—159).—When a snail lichenase preparation is preserved, its activity gradually diminishes in the course of about 14 days by some 30%, and then remains constant for a long period. The change is shown to be due to the disappearance of cellobiase, a constituent enzyme. Whereas fresh lichenase decomposes lichenin or cellobiose completely to dextrose, lichenase which has been preserved only carries the decomposition of lichenin to an intermediate stage, probably to cellobiose.

E. H. R.

Serum Lipase. G. Fanconi (*Fermentforsch.*, 1924, **7**, 307—348).—Some hydrolysis of fats and cholesterol esters is shown to occur in human serum. Since the tributyrinase of serum (the so-called serum lipase) can be extracted in part by fats and lipoids, and since in lipæmic serum the lipolytic activity is less than in that from the fasting animal, it is argued that the tributyrinase is probably identical with the fat-splitting agent of the serum. The view that serum lipase and complement are closely related is not supported by the fact that quinine and atoxyl inhibit the lipolytic activity but not the complement function of serum. The variations in the lipolytic activity of serum in physiological and pathological conditions are described. R. K. C.

Action of Arsenic and Antimony Compounds on the Fermentative Functions of the Organism. II. Action of certain Arsenic and Antimony Preparations on Pepsin. J. A. Smorodincev and N. P. Riabouschinsky (*Biochem. Z.*, 1924, **144**, 26—30).—Sodium and potassium arsenites and arsenates, and potassium antimonyl tartrate retard the action of pepsin on casein, the last-mentioned in $N/50$, the others in $N/40$ solutions. Lower concentrations of these salts from $N/80$ to $N/10240$ have no influence on the activity of pepsin. In contrast to ptyalin (A., 1923, i, 1246), pepsin is not so susceptible to antimony as to arsenic, and is more stable to both types of compound than is the former enzyme. Hydrochloric acid ($N/40$ to $N/1600$) and tartaric acid ($N/10$ to $N/1280$) have no influence on the action of pepsin. J. P.

Adsorption of Trypsin by Filter-paper. Tsou-Hia Hsü (*Biochem. Z.*, 1924, **144**, 303—307).—Trypsin (Merck) is adsorbed from solution by various makes of filter-paper (Schleicher and Schüll, Dreverhoff). The adsorbed enzyme may be partly recovered by washing with dilute sodium hydroxide and with phosphate solutions of p_H 6·6 to 7·6. Washing with acid, sodium carbonate, and ammonia is ineffective. Variations in temperature have little or no effect on the extent of the adsorption. J. P.

Influence of Colloids on Enzymes. III. I. Hagihara (*Biochem. Z.*, 1924, **144**, 482—489).—Cholesterol has no influence on the action of trypsin at the hydrogen-ion concentration range p_H 5·3—p_H 10·6. Lecithin, on the other hand, stimulates the action of the enzyme in proportion to the quantity present. This stimulation occurs only in alkaline solutions, being entirely absent at or below p_H 6·8; it reaches its maximum at p_H 7·6 and falls in more alkaline solutions. S. S. Z.

Kinetics of Trypsin Digestion. I. Experimental Evidence Concerning the Existence of an Intermediate Compound. J. H. Northrop (*J. Gen. Physiol.*, 1924, **6**, 239—243).—If, as has been suggested, a compound is formed between trypsin and its substrate, the presence of gelatin should decrease the rate of hydrolysis of casein, but this was found not to be the case. This result cannot be explained on the hypothesis that different enzymes in the trypsin act on the two proteins, since the presence of casein, or of gelatin, inhibits the heat-inactivation of the gelatin-hydrolysing power, or of the casein-hydrolysing power, respectively, of the trypsin used (Fairchild's). W. O. K.

Test for Diffusible Ions. I. Ionic Nature of Trypsin. J. H. NORTHROP (*J. Gen. Physiol.*, 1924, **6**, 337—347).—The ratio of the concentrations of trypsin inside and outside the particles of gelatin suspended in water, is equal to the ratio of the hydrogen-ion concentrations on the two sides between the limits of p_H 2 to 10·2. Above p_H 10·2 the trypsin is distributed in the same ratio as the chlorine ion. Trypsin would therefore appear to be a diffusible amphoteric electrolyte, with isoelectric point at p_H 10·2, giving positive univalent ions below this value and negative univalent ions above it, and to be distributed on the two sides of the surface of the gelatin particles in accordance with the Donnan equilibrium. It would seem to be a strong base below p_H 10·2, as no evidence was obtained of undissociated trypsin. With increasing salt content, the same relations in the concentrations hold. The ratios of the concentrations of trypsin, and of hydrogen- and chlorine-ions all change in accordance with the Donnan equilibrium. W. O. K.

[**Pancreatic Enzymes. V.** R. WILLSTÄTTER and collaborators.] **Enterokinase and the Tryptic Action of the Pancreas.** E. WALDSCHMITZ-LEITZ (*Z. physiol. Chem.*, 1924, **132**, 181—237).—A detailed investigation of the influence of enterokinase on the tryptic hydrolysis of gelatin in which the tryptic activity was determined by a method based on that of Willstätter and Waldschmitz-Leitz (cf. A., 1922, ii, 169). The activation of trypsinogen by the kinase is, in its initial stages, proportional to the time and reaches a constant value, less than the maximum possible degree of activation, in from 30 to 60 minutes according to the amount of kinase present. The speed of activation is greatest in neutral solutions. For any given preparation there is a direct proportionality between the amount of kinase necessary for the final degree of activation attained, and the amount of the enzyme activated. Glycerol and ethylene glycol and substances of autolytic origin have an inhibiting effect on the activation. The preparation of purified enterokinase free from proteolytic enzymes is described. Such preparations are highly specific and have no influence on pancreatic lipase or diastase. The author interprets his results as pointing to a simple activation of trypsinogen by the kinase, and as opposing the view that the process is an enzymic one. Using alumina as adsorbent, it is possible to separate the enzyme and its activator and so convert an active trypsin preparation into an inactive trypsinogen, which may then be subsequently reactivated. The trypsinogen of fresh or dried pancreas becomes "spontaneously" activated on keeping, especially in acid solution. This is regarded not as an autolytic change of the inactive enzyme, but as analogous to the activation by enterokinase, since, like the latter, the substance responsible for the phenomenon may be adsorbed by alumina and so separated from an active trypsin which is thus reconverted to trypsinogen. The possible identity of this "spontaneous" activator with enterokinase is discussed in relation to the secretion of active pancreatic juice under the influence of pilocarpine and peptone. It is concluded that the activation of trypsinogen by enterokinase is a specific reaction conditioned in part by adsorption, but chiefly by the mutual influence of enzyme and activator on the affinities of specific groups, which is likened to the effect of hydrogen-ion concentration. J. P.

Arginase in Bacteria. S. HINO (*Z. physiol. Chem.*, 1924, **133**, 100—115).—Living *Bacillus pyocyaneus* and *B. fluorescens*, as well as their acetone preparations, act on *d*-arginine. Filtrates from their cultures were inactive. The arginase is more active in the living organisms. The presence of urease in the above organisms has also been established. *Staphylococci*, *B. prodigiosus*, *B. coli*, *B. paratyphosus*, *B. typhosus*, *B. dysenteriæ* (Shiga), and *Streptococci* do not contain arginase. S. S. Z.

Preparation of Dried Urease and Determination of Urea in Normal and Pathological Urines. G. REVOLTELLA (*Biochem. Z.*, 1924, **144**, 229—257).—Improvements are given in the method already described by the author (*ibid.*, 1922, **134**, 336) for preparing dried urease from soya beans. A correction factor of 5·3% must be added to the urea determined by means of urease prepared by the author's old method in view of the incomplete nature of the conversion of urea to ammonium carbonate. Two improved methods for determining urea are described. In the direct method, 5 c.c. of urine and 2 drops of 0·3% methyl-orange are placed in each of two 50-c.c. graduated flasks, and 0·05*N*-sulphuric acid is added until the colour is light orange; 0·25—1·0 g. of urease (according to the activity of the preparation) is added, the solutions are diluted to 50 c.c. with distilled water, and the flasks are stoppered and placed in a water-bath for 1 hour at 45—50°. Ten c.c. of solution from one flask are titrated against 0·05*N*-sulphuric acid to a light orange and the number of c.c. of acid required multiplied by 0·15525 gives the corrected urea content in grams per 100 c.c. The second flask serves as a control on the completion of the fermentation. An improved direct aspiration method for determining the preformed ammonia and urea in urine or in any body fluid is also given, for details of which the original must be consulted. The influence of various normal and pathological constituents of urine, such as uric acid, proteins, amino-acids, dextrose, sodium chloride, and ammonium carbonate, and of varying conditions of temperature, hydrogen-ion concentration, and light, on the urease method of determining urea has been studied. It is concluded that urease methods provide, when properly controlled, the most convenient and most accurate means of determining urea. J. P.

Auxoureases. F. DI RENZO (*Biochem. Z.*, 1924, **144**, 298—302).—Preliminary heating of a solution of urease for periods varying from 10 to 30 minutes increases the activity of the enzyme, the maximum effect being attained with temperatures of 60—70° using 0·3% solutions of urease. The phenomenon is regarded as being similar to the activating effect of "auxo" bodies such as potassium cyanide and glycine on urease. J. P.

Sulphatase. IV. Enzymic Fission of β-Naphthyl Hydrogen Sulphate. J. NOGUCHI (*Biochem. Z.*, 1924, **144**, 138—140).—β-Naphthyl potassium sulphate was prepared by treating β-naphthol in the presence of pyridine with chlorosulphonic acid dissolved in chloroform, followed by removal of the solvents and neutralisation with potassium hydroxide. The potassium salt, obtained as fine white plates, gave no precipitate in aqueous solution with barium chloride. On incubation with sulphatase (A., 1923, i, 1148; 1924, i, 107), it is hydrolysed to β-naphthol and potassium sulphate.
J. P.

Acid Production by *Bac. Granulobacter*. H. B. SPEAKMAN. —(See i, 371.)

Isoelectric Points for the Mycelium of Fungi. W. J. ROBBINS (*J. Gen. Physiol.*, 1924, **6**, 259—271; cf. *Amer. J. Bot.*, 1923, **10**, 412).—Mycelia of *Rhizopus nigricans* and of *Fusarium lycopersici* behaved towards acid and basic dyes similarly to amphoteric colloids with isoelectric points p_H 5·0 and 5·5 respectively. The amount of growth of *Rhizopus nigricans* on potato-dextrose agar and also the dry matter produced when grown on potato-dextrose broth, when plotted against the p_H of the medium, show a double maximum with an intervening minimum at initial p_H 5·2. W. O. K.

Assimilation of Aldehydes by Plants. II. Polymerisation of Formaldehyde by *Phaseolus multiflorus* and *Pelargonium* with the Formation of Higher Aldehydes. T. SABALITSCHKA and H. RIESENBERG (*Biochem. Z.*, 1924, **144**, 545—550).—The above plants assimilate formaldehyde in the dark with the formation of sugar and starch. S. S. Z.

Assimilation of Aldehydes by Plants. III. Does the Presence of Formaldehyde interfere with the Determination of Sugar and Starch in the Experimental Plants of T. Sabalitschka? T. SABALITSCHKA and H. RIESENBERG (*Biochem. Z.*, 1924, **144**, 551—555).—It does not. S. S. Z.

Respiratory Quotient of Roots and its Variation with the Development of the Plant. R. CERIGHELLI (*Compt. rend.*, 1924, **178**, 645—647).—The respiratory quotient for the detached roots of various plants has been determined at different periods of growth. It was always found to be less than unity at the beginning of growth, and with annuals poor in reserve materials (wheat, maize, etc.), it remains so throughout the whole of the growth period. These two facts are the reverse of those observed in the case of the leaves.

As previously found, the respiratory quotient often falls at the time of flowering or of fruit-bearing, or at some time after this. The root in this case behaves analogously to the leaves.

Annuals possessing plentiful reserve materials (radish, lupin, etc.) and most perennials (iris, rhubarb, etc.) give a respiratory quotient greater than unity, except at the beginning of the growth period. E. E. T.

Effect of Phosphates on [Plant] Respiration. C. J. LYON (*J. Gen. Physiol.*, 1924, **6**, 299—306).—The effect of increasing the phosphate content of the medium upon which *Elodea canadensis* is growing is to increase within about 30 minutes the rate of respiration as measured by the production of carbon dioxide. This effect increases with the concentration of phosphate-ion up to a concentration of $0{\cdot}1M$, beyond which it remains constant. When plotted against time it is found that for any given phosphate concentration the rate of respiration rises to a maximum, falls, rises to a second higher maximum, and again falls. The death of the plant occurs during the fall from the first maximum, the subsequent respiration being a *post-mortem* phenomenon. To investigate the anaërobic respiration wheat seedlings were used, and a similar increase in the production of carbon dioxide in the presence of phosphate was observed. W. O. K.

Development of Pentosans in Barley during Germination. M. H. VAN LAER and A. MASSCHELEIN (*Bull. Soc. chim. Belg.*, 1923, **32**, 402—404).—During the germination process a distinct increase in the quantity of pentosans occurs in barley, especially in the embryo and the radicles. The endosperm also shows an appreciable increase. On steeping in water the total pentosan loss is about 4%; this takes place almost entirely from the chaff. Malting also results in the formation of pentosans, but in this case the distribution is not similar, the increase being considerable in the endosperm, whilst it is very small in the radicles. H. J. E.

Absorption of Carbon by the Roots of Plants. J. F. BREAZEALE (*J. Agric. Res.*, 1923, **26**, 303—311).—Wheat seedlings were grown in a number of different culture solutions, and the plant ashes examined. Carbonates were found in the ash of plants grown in solutions containing sodium or ammonium nitrate, or the carbonates of calcium, sodium, or potassium. The carbonate ion was absorbed by the roots of the plants, but free carbon dioxide could not be taken up in the absence of soluble bases; the rate of absorption of bases depended largely on the absorption of an acid radical. It is suggested that such salts as sodium nitrate influence carbonate absorption as a result of the more rapid removal of the nitrate ion and the subsequent formation of sodium carbonate from atmospheric carbon dioxide. Evidence is advanced that the so-called "lime-loving" plants are in reality those requiring considerable amounts of carbonate. The plant root may maintain equilibrium in its tissues or in the nutrient solution by the intake of carbonate ions or by the excretion of free carbon dioxide. A. G. P.

The Form of Nitrogen most Favourable for Higher Plants. G. Truffaut and N. Bezssonoff (*Compt. rend.*, 1924, **178**, 723—725).—An investigation of the effect of various nitrogenous fertilisers on the growth of several common crops in pots and in the field. It is concluded that mixtures containing nitrogen in the form of carbamide are more effective than nitrates, ammonium salts, or even carbamide alone. In acid soils, carbamide–sodium nitrate mixtures, in alkaline soils, carbamide–ammonium sulphate mixtures, appeared to give the best result. In some cases mixtures of this type have enabled the authors to reduce the percentage of nitrogen in the fertiliser from 3% to 2% and yet to obtain an increased yield. E. E. T.

Influence of a Deficiency of Potash on the Development of Barley Manured with different Amounts of Sodium Nitrate. H. Weissmann (*Z. Pflanz. Düng.*, 1924, **A**, **3**, 21—24).—Barley was grown in sand cultures, with a potash-free nutrient solution, to which increasing amounts of sodium nitrate were added. The dry-weight of the crop decreased with increasing amounts of sodium nitrate, only those plants having the smallest amount of sodium nitrate in the nutrient reaching the grain stage. The other plants died prematurely. The total intake of potassium by the plants decreased with larger doses of sodium nitrate, but the nitrogen- and sodium-intake increased with the proportion of sodium nitrate in the nutrient. The bearing of these results on the influence of potash-starvation on growth (cf. *ibid.*, 1923, **A**, **2**, 1) is discussed. A. G. P.

Coexistence of Starch and Inulin in certain *Compositæ*. L. Daniel (*Compt rend.*, 1924, **178**, 726—727).—Starch and inulin have been found to occur together in *Helianthus tuberosus* and *H. multiflorus* grafted on to the sunflower (annual). On one occasion they were both found in an artichoke graft. They were also found in ungrafted plants, *e.g.*, *Jurinea alata* and various species of *Centaurea*. E. E. T.

State of Tannins in the Vegetable Cell. Michel-Durand (*Compt. rend.*, 1924, **178**, 586—589).—Young oak or chestnut plants, on being extracted with acetone, yield, in general, less tannin than when extracted with boiling water. It is concluded that the tannin is present, in the cell, in more or less intimate combination with mucilaginous substances. E. E. T.

Protopectin and some other Constituents of Lemon Peel. R. Sucharipa (*J. Amer. Chem. Soc.*, 1924, **46**, 145—156).—The author distinguishes between "free pectin," the soluble jelly-making portion of fruits etc.; "protopectin," the water-insoluble pectin occurring in the cell wall closest to the cellulose layer; and "pectic acid," the ultimate product of hydrolysis of pectic substances. Protopectin was prepared from the white pericarp of *Citrus limonum*. It gave pectin and cellulose on hydrolysis besides a small amount of impurities, including lignocelluloses that could not be removed previously. Pectins with different methoxyl contents have been prepared from the same source. It has been shown that the cell-wall of the parenchymatous tissue of *Citrus* contains " free " cellulose, which dissolves readily in Schweitzer's reagent, and also cellulose combined with pectin, which becomes soluble only after hydrolysis. An hypothesis is advanced as to the linking of the cellulose and pectin, based on the replacement of the cellulose in protopectin by methoxyl groups. The question of the transition of protopectin to pectin in the cell is discussed. F. A. M.

Constitution of Derris Root. I. S. Takei (*Rikwagaku Kenkyujo Ihô*, 1923, **2**, 485—496; cf. Kariyone and Atsumi, A., 1923, i, 477).—When extracted with hot ether, roots of *Derris elliptica*, Benth., grown in Singapore, gave colourless, hexagonal plates, m. p. 163°, which correspond with tubatoxin; the formula was found to be $C_{19}H_{18}O_5$, whilst former investigators gave $C_{18}H_{18}O_5$. Its methoxyl content corresponded with 1·5 methoxy groups in 1 mol.; it gave a phenylhydrazone, yellow needles, m. p. 243—245°. For the rabbit, the minimum lethal dose was 0·00125 g. per 100 g. of body-weight. When treated with concentrated sulphuric acid, it was changed into an *isomeride*, colourless needles, m. p. 177—178°, having no poisonous properties. The saponification of tubatoxin with 3% hot alcoholic potash gave a *phenolcarboxylic acid*, $C_{10}H_{10}O_3$, m. p. 128—129°, which absorbed bromine and gave a violet colour with ferric chloride. When the saponification was conducted in a current of hydrogen, an *isomeride*, colourless needles, m. p. 209—210°, was obtained which had no poisonous action. By fusion with potassium hydroxide, tubatoxin itself or the acids mentioned above gave another *phenolcarboxylic acid*, $C_9H_9O_3$, colourless needles, m. p. 182°. This acid sublimed at about 160°, and is probably a methylated benzoic acid. K. K.

Chemical Analysis of *Jatropha stimulosa*. P. Menaul (*J. Agric. Res.*, 1923, **26**, 259—260).—The seeds of *Jatropha stimulosa* resemble castor beans, and contain 61% of kernel. The expressed oil had the following characteristics: $d^{15\cdot6}$, 0·9257; $n^{15\cdot6}$, 1·4765; solidifies below − 15°; iodine number, 124·65—129·47; saponification number, 186; volatile fatty acids, none; free fatty acids, trace; fatty acids, 95·6%; glycerol about 4·2%. The seeds also contain much protein, the analysis and nitrogen distribution of which has been studied. There is a high histidine content. A. G. P.

Mono- and Di-methylolcarbamide. Their Effect on Plant Growth, and their Decomposition in the Soil. E. Blanck and F. Giesecke (*Z. Pflanz. Düng.*, 1923, **2**, 393—420).—When formaldehyde is added as a preservative to liquid manure (urine) containing carbamide, monomethylol carbamide, $CO(NH_2)NH{\cdot}CH_2{\cdot}OH$, and dimethylolcarbamide, $CO(NH{\cdot}CH_2{\cdot}OH)_2$, may be formed. Experiments are described on the effect of these compounds, and also of liquid manure–formaldehyde mixtures, on the growth of plants in sand and soil cultures. Both compounds at first depress the germination of oats and turnips. This effect is, however, followed by stimulation. Monomethylolcarbamide is equally effective with ammonium sulphate as a source of nitrogen for oats and mustard. Dimethylolcarbamide is generally less satisfactory, and may in some cases be actually harmful. The experiments with liquid manure–formaldehyde mixtures show similar results, large amounts of formaldehyde being injurious. The nitrogen of these compounds is readily ammonified by soil organisms. It is concluded that whilst formaldehyde may be used as a preservative with liquid manure, excess should be avoided. G. W. R.

Nature of the Activity of the Colloidal Clay of Acid Soils. R. Bradfield (*J. Amer. Chem. Soc.*, 1923, **45**, 2669—2678).—In this investigation, standard solutions of sodium hydroxide and calcium hydroxide were titrated with the colloidal material from four acid soils and the end-points determined by both conductivity and hydrogen-ion concentration measurements (cf. *ibid.*, 1923, **45**, 1245). The end-points found by both methods were fairly definite, and the titration curves were of the type commonly obtained in the titration of a strong base by a weak acid. The same amounts of the colloidal acids were required to neutralise equivalent quantities of the two bases, and definite breaks were obtained in the conductivity curves, indicating the neutralisation of definite acids. The reaction between acid colloidal clays and strong bases appears to be an ordinary neutralisation. The results obtained tend to show that the colloidal material of an acid soil is itself an acid which ionises to produce a definite Sörensen value and which shows a definite titrable acidity on titration with strong bases. F. G. P.

Soil Reaction in Relation to Calcium Adsorption. C. O. Swanson (*J. Agric. Res.*, 1923, **26**, 83—121).—The adsorption of calcium and the alterations in soil reaction, following the addition of lime to a number of soils, are described. Potassium chloride was found to reduce the adsorption of calcium in soils unless relatively large amounts of calcium carbonate were present. Soil suspensions showed lower p_H values than filtered soil extracts. The adsorption of calcium by soils was more intimately connected with the clay content than with the original hydrogen-ion concentration of the soil. Fuller's earth had a greater hydrogen-ion concentration and a greater adsorptive power than any soil examined. Leaching with water did not affect the adsorptive power or p_H value of soils. The presence of calcium carbonate did not influence the calcium adsorption from calcium hydroxide. Dilute hydrochloric acid increased the hydrogen-ion concentration of soils to an extent proportional to the amount of acid. Small additions of oxalic acid to soil decreased the hydrogen-ion concentration and larger amounts increased this figure, but to a less extent than did equivalent quantities of hydrochloric acid. Acidity of mineral soils is attributed to the leaching out of bases leaving acid alumino-silicates, which readsorb soluble bases (particularly calcium), leaving an insufficient supply for the normal growth of plants. A new apparatus for determining hydrogen-ion concentrations of soils is described. A. G. P.

Partial Sterilisation of Soil by Antiseptics. (Mrs.) A. Matthews (*J. Agric. Sci.*, 1924, **14**, 1—57).—An examination is recorded of the microflora in soils treated with a number of organic antiseptics. The normal effect of antiseptics—an initial decrease in bacterial numbers followed by a sudden rise, which was maintained for varying periods and finally tended to return towards normal—was observed. The antiseptics disappeared from the soil fairly quickly. Aëration increased the rapidity of these changes. The extent of the increase in bacterial numbers varied according to the molecular weight and heat of combustion of the antiseptics used, and some correlation with the latter factor is indicated. Bacterial changes seemed in no way connected with protozoa and occurred in a normal manner even in protozoa-free soils. Increases in bacterial population are ascribed to the feeding effect of the antiseptics or the bacteria, and the improved fertility following partial sterilisation to the breaking down of soil organic matter by the increased number of organisms. The action of lime and of steaming in increasing the bacteria is assumed to result from improved conditions, due to the breaking down of plant residues, etc. Aliphatic compounds produce quicker but smaller changes than aromatic ones. Among aromatic compounds, the introduction of the $-CH_3$ group into the benzene ring lessened the toxicity of the compound to soil organisms, whereas $-Cl$ and $-NO_2$ produced increased toxicity and stability in the soil. The toxic effects of a number of antiseptics on protozoa, eelworm, and fungi are recorded.

A. G. P.

The Manurial Properties of Lead Nitrate. R. A. Berry (*J. Agric. Sci.*, 1924, **14**, 58—65).—A number of culture and field experiments are described in which lead nitrate was used as the source of nitrogen to plants, in comparison with sodium nitrate. Similar yields were obtained by both treatments. The lead salt tended to produce plants with wider leaf blade and of slightly darker colour. When used in commercial quantities, no lead was found in the plants produced, nor could any be leached from the soil. Except when high concentrations were used, lead was adsorbed and rendered non-toxic by the soil. It would appear probable that lead salts increased the rate of nitrification in soils.

A. G. P.

Action of Sodium Nitrite in the Soil. R. H. Robinson (*J. Agric. Res.*, 1923, **26**, 1—7).—Experiments are described demonstrating the unsuitability of sodium nitrite as a fertiliser, particularly on acid soils. In all soils examined, there was a steady loss of nitrogen from the nitrite, only a small proportion of which became oxidised to nitrate. This loss was much accelerated in acid soils. The addition of lime or calcium carbonate to such soils retarded the decomposition of nitrites, but no increased nitrate content could be observed.

A. G. P.

Organic Chemistry.

Silver-sulphochromic Oxidation of Coal. L. J. Simon (*Compt. rend.*, 1924, **178**, 775—777).—When coal is heated with a mixture of silver dichromate and concentrated sulphuric acid at 100°, 4—5% of the carbon present remains unoxidised. Formation of gaseous oxidation products is more rapid at 50° than at 60°, at which temperature 28% of the coal remains unchanged, about 6·7% being rendered soluble. When powdered coke is oxidised by chromic acid, 54·2% is unaffected, as against 39% when silver dichromate is used. It is concluded from the results that coal contains two constituents intimately mixed. One is oxidised at low temperatures, the other, like coke, requiring a temperature of 100°. E. E. T.

Composition of Natural Gas Gasoline. R. P. Anderson and A. M. Erskine (*J. Ind. Eng. Chem.*, 1924, **16**, 263—267).—Fractional distillation shows that the approximate composition of this gasoline is: propane and butanes, 20% (by volume); *iso*pentane, 13%; *n*-pentane, 17%; *iso*hexane, 9%; *n*-hexane, 15%; *iso*heptane, 8%; *n*-heptane, 12%; octane, 4%, and absorption oil, 2%; the presence of traces of benzene and toluene is indicated. C. I.

Composition of Low-temperature Tar. IV. F. Schütz, W. Buschmann, and H. Wissenbach (*Ber.*, 1924, **57**, [*B*], 421—423; cf. A., 1923, i, 1080).—An examination of the requisite C_9 to C_{12} fraction of neutral oil from low-temperature coal-tar showed that 80—86% consists of unsaturated and aromatic hydrocarbons, whilst the remaining 14—20%, boiling from 30° to 220°, probably contains *n*-nonane, *n*-decane, *n*-undecane, and *n*-dodecane, as indicated by the boiling points of the fractions, although the densities are slightly too high. [Cf. *B.*, 1924, 367.] F. A. M.

Action of Sodamide on True Acetylene Hydrocarbons. Bourguel (*Compt. rend.*, 1924, **178**, 777—779; cf. A., 1923, i, 1176).—When chloro-compounds are treated, by the author's method, with sodamide, the acetylene hydrocarbon is never present as such at the end of the reaction, but as a sodamide or sodium derivative of the hydrocarbon. If pure pentinene, diluted with xylene, is added to a xylene suspension of sodamide heated at 120°, 1 mol. of ammonia is evolved per mol. of pentinene, with formation of a sodium derivative of the latter. E. E. T.

Chlorination of Butylene and the Properties of Dichlorobutane. E. Briner, J. Hausser, and E. de Luserna (*Helv. Chim. Acta*, 1924, **7**, 374—376).—*n*-Butyl alcohol is readily converted into butylene by passage over alumina at 480°. Butylene combines with chlorine, with evolution of heat, forming dichlorobutane, the molecular heat of reaction being 33·4 Cal. The reaction is not explosive. Dichlorobutane has b. p. 114·6—114·8°/730 mm.; n^{20} 1·4325; d^{0} 1·144, $d^{22\cdot2}$ 1·115, $d^{99\cdot5}$ 1·032; ignition temperature, 62°. The viscosity coefficient is 0·0515 at 0°, 0·01073 at 22·2°, 0·00535 at 99·5°. It is a good solvent for oils and fats and is not poisonous. E. H. R.

Action of Ammonia on Organic Halogen Compounds at High Temperature. J. Heslinga (*Rec. trav. chim.*, 1924, **43**, 178—180).—The halogen in organic compounds containing chlorine or bromine is quantitatively converted into ammonium halide when the substance is heated to redness in a current of ammonia. Chloro derivatives of benzene, if substituted in the ring, are exceptions to the general rule. (Cf. this vol., ii, 55.) H. J. E.

Near Ultra-red Absorption Spectra of some Organic Liquids. J. W. Ellis.—(See this vol., ii, 218.)

Analogues of Citronellol Richer and Poorer in Carbon. I. J. von Braun and R. Gossel (*Ber.*, 1924, **57**, [*B*], 373—382).—The effect of the position of the double bond and of the number and position of the methyl groups on the odour of citronellol, $CMe_2{:}CH\cdot[CH_2]_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH$, has been examined. The conversion of the terminal group, $CMe_2{:}C-$, into the complex, $CH_2{:}C-$, causes a very marked alteration in odour which is less marked when the group is $CHMe{:}C-$; the introduction of further methyl radicals (in addition to the γ-methyl group) does not cause an appreciable change in odour, whence it is probable that the γ-methyl group is itself unimportant. The decisive factor appears to be the presence of the group $CMe_2{:}C-$, or to a less extent of $CHMe{:}C-$, at a definite distance from the primary alcoholic group. The alcohols described in the present communication are optically inactive, but the comparison of them with optically active citronellol is regarded as justifiable, since, in general, little difference in odour is observed between isomeric active and racemic substances.

Δ^{β}-Butenyl bromide reacts readily with an alcoholic solution of ethyl sodioacetoacetate to give a mixture of *ethyl butenylacetoacetate*, $CH_3\cdot CO\cdot CH(CH_2\cdot CH{:}CHMe)\cdot CO_2Et$, a mobile liquid, b. p. 112—114°/11 mm., and *ethyl dibutenylacetoacetate*, b. p. 135—137°/12 mm. The former ester is hydrolysed by dilute, aqueous potassium hydroxide solution to *Δ^{β}-heptene-ζ-one*, $CHMe{:}CH\cdot[CH_2]_2\cdot COMe$, b. p. 152—155°/atmospheric pressure, 42—43°/9 mm., d_4^{20} 0·8446, n_D^{20} 1·4292 (*semicarbazone*, lustrous leaflets, m. p. 97°). *Ethyl methylbutenylacetoacetate*, $CH_3\cdot CO\cdot CMe(CH_2\cdot CH{:}CHMe)\cdot CO_2Et$, b. p. 120—122°/20 mm., is hydrolysed to *γ-methyl-Δ^{ϵ}-heptene-β-one*, $CHMe{:}CH\cdot CH_2\cdot CHMe\cdot COMe$, b. p. 62—64°/20 mm., d_4^{18} 0·8463, n_D^{18} 1·4345, which resembles amyl acetate in odour.

Ethyl β-methyl-$\Delta^{\alpha\epsilon}$-heptadienoate, a colourless liquid, b. p. 103—105°/22 mm., prepared by the action of potassium hydrogen sulphate at 150° on ethyl β-hydroxy-β-methyl-$\Delta^{\alpha\epsilon}$-heptadienoate, is reduced by sodium and alcohol to *γ-methyl-Δ^{ζ}-heptenol*,

$$\mathrm{CH_2{:}CH\cdot[CH_2]_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH},$$

b. p. 97—99°/22 mm., d_4^{19} 0·8562, n_D^{19} 1·4470, which has no resemblance in odour to citronellol.

Δ^{β}-Hexene-ζ-one is transformed by zinc and ethyl α-bromopropionate into *ethyl β-hydroxy-αβ-dimethyl-Δ^{ϵ}-heptenoate*,

$$\mathrm{CH_2{:}CH\cdot[CH_2]_2\cdot CMe(OH)\cdot CHMe\cdot CO_2Et},$$

a somewhat viscous, colourless, odourless liquid, b. p. 124—126°/18 mm., which is hydrolysed to the corresponding *acid*, a colourless, viscous liquid with a very unpleasant odour, b. p. 175—176°/18 mm. The latter compound is converted by acetic anhydride and anhydrous sodium acetate into *αβ-dimethyl-$\Delta^{\alpha\epsilon}$-heptadienoic acid*,

$$\mathrm{CH_2{:}CH\cdot[CH_2]_2\cdot CMe{:}CMe\cdot CO_2H},$$

an unpleasant smelling liquid, b. p. 145—146°/18 mm., from which *ethyl αβ-dimethyl-$\Delta^{\alpha\epsilon}$-heptadienoate*, b. p. 103—105°/18 mm., is prepared. The ester is reduced by sodium and alcohol to *βγ-dimethyl-Δ^{ζ}-heptenol*, $\mathrm{CH_2{:}CH\cdot[CH_2]_2\cdot CHMe\cdot CHMe\cdot CH_2\cdot OH}$, b. p. 101—102°/20 mm., d_4^{21} 0·8741, n_D^{21} 1·4570, the odour of which is quite distinct from that of citronellol.

Ethyl β-hydroxy-αβγ-trimethyl-Δ^{ϵ}-heptenoate,

$$\mathrm{CH_2{:}CH\cdot CH_2\cdot CHMe\cdot CMe(OH)\cdot CHMe\cdot CO_2Et},$$

a viscous liquid with a very faint odour, b. p. 123—125°/17 mm., is readily obtained from γ-methyl-Δ^{ϵ}-heptene-β-one, zinc, and ethyl α-bromopropionate. Complete dehydration of this compound or of the corresponding hydroxy acid could not be accomplished. The incompletely homogeneous βγδ-trimethyl-Δ^{ζ}-heptenol,

$$\mathrm{CH_2{:}CH\cdot CH_2\cdot[CHMe]_3\cdot CH_2\cdot OH},$$

does not, however, resemble citronellol in odour.

Ethyl β-hydroxy-β-methyl-Δ^{ϵ}-octenate,

$$\mathrm{CHMe{:}CH\cdot[CH_2]_2\cdot CMe(OH)\cdot CH_2\cdot CO_2Et},$$

b. p. 121—122°/10 mm., is hydrolysed to the corresponding *acid*, a viscous liquid, b. p. 177—180°/16 mm., which is transformed by sodium acetate and acetic anhydride into *β-methyl-$\Delta^{\alpha\epsilon}$-octadienoic acid*, $\mathrm{CHMe{:}CH\cdot[CH_2]_2\cdot CMe{:}CH\cdot CO_2H}$, b. p. 149—150°/18 mm., from which *ethyl β-methyl-$\Delta^{\alpha\epsilon}$-octadienoate*, b. p. 114—115°/18 mm., is obtained. The ester is readily reduced by sodium and alcohol to *γ-methyl-Δ^{ζ}-octenol* (*norcitronellol*),

$$\mathrm{CHMe{:}CH\cdot[CH_2]_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH},$$

b. p. 109—111°/20 mm., d_4^{20} 0·8674, n_D^{20} 1·4560, which has a terpene-like odour with a faint resemblance to that of citronellol. β-*Methyl-Δ^{ϵ}-octenoic acid*, $\mathrm{CHMe{:}CH\cdot[CH_2]\cdot CHMe\cdot CH_2\cdot CO_2H}$, b. p. 145—146°/18 mm., is obtained as by-product of the reduction; the corresponding *ethyl* ester has b. p. 109—111°/21 mm.

Ethyl β-hydroxy-αβ-dimethyl-Δ^{ϵ}-octenoate,

$$\mathrm{CHMe{:}CH\cdot[CH_2]_2\cdot CMe(OH)\cdot CHMe\cdot CO_2Et},$$

b. p. 139—142°/20 mm., is converted by potassium hydrogen sulphate into *ethyl αβ-dimethyl-$\Delta^{\alpha\epsilon}$-octadienoate*,

$$\mathrm{CHMe{:}CH\cdot[CH_2]_2\cdot CMe{:}CMe\cdot CO_2Et},$$

a liquid with a tolerably pleasant odour, b. p. 115—116°/19 mm., and the corresponding *acid*, an unpleasant smelling liquid, b. p.

152—155°/20 mm. The ester is reduced by sodium and alcohol to *βγ-dimethyl-Δ^{ζ}-octenol*, $CHMe\colon CH\cdot[CH_2]_2\cdot[CHMe]_2\cdot CH_2\cdot OH$, b. p. 111—112°/21 mm., d_4^{21} 0·8775, n_D^{21} 1·4670, which resembles the terpenes and citronellol in odour.

Ethyl β-hydroxy-βγ-dimethyl-Δ^{ϵ}-octenoate,

$$CHMe\colon CH\cdot CH_2\cdot CHMe\cdot CMe(OH)\cdot CH_2\cdot CO_2Et,$$

an odourless liquid, b. p. 137—139°/20 mm., is transformed successively into *ethyl βγ-dimethyl-$\Delta^{\alpha\epsilon}$-octadienoate*, a very pleasant smelling liquid, b. p. 123—124°/20 mm., and *γδ-dimethyl-Δ^{ζ}-octenol*, $CHMe\colon CH\cdot CH_2\cdot[CHMe]_2\cdot CH_2\cdot CH_2\cdot OH$, b. p. 114—115°/17 mm., d_4^{19} 0·8775, n_D^{19} 1·465, which is allied to citronellol in odour.

Methylheptenone, zinc, and ethyl α-bromopropionate yield *ethyl β-hydroxy-αβζ-trimethyl-Δ^{ϵ}-octenoate*,

$$CMe_2\colon CH\cdot[CH_2]_2\cdot CMe(OH)\cdot CHMe\cdot CO_2Et,$$

a colourless, viscous liquid, b. p. 145°/16 mm., which is transformed by potassium hydrogen sulphate at 150° into *ethyl αβζ-trimethyl-$\Delta^{\alpha\epsilon}$-octadienoate*, b. p. 126—128°/20 mm. The latter ester is smoothly reduced to *βγη-trimethyl-Δ^{ζ}-octenol* (*homocitronellol*),

$$CMe_2\colon CH\cdot[CH_2]\cdot[CHMe]_2\cdot CH_2\cdot OH,$$

a mobile liquid, b. p. 125—127°/20 mm., d_4^{17} 0·8860, n_D^{17} 1·4725. The odour of the substance is more closely similar to that of citronellol than are those of the alcohols containing the terminal group, $CHMe\colon C-$. When preserved, it exhibits the same change and refinement of odour which is characteristic of citronellol, and is possibly due to an establishment of an equilibrium between two forms containing the groups, $CMe_2\colon C-$ and $CH_2\colon CMe\cdot C-$. H. W.

Manufacture of Ether. J. DESMAROUX (*Mém. Poudres*, 1923, **20**, 335—390).—The system, $H_2SO_4–EtOH–H_2O–Et_2O–EtHSO_4$, is considered theoretically, and a diagram is evolved showing the interdependence of the concentrations of the various components. Phase-rule considerations show that the system has three degrees of freedom. The state of equilibrium, particularly with regard to ether, is practically independent both of the temperature and of the sulphuric acid concentration. The experimental results obtained are in excellent agreement with the formulæ $Y=m(1-10^{-ht})$ and $X=r(1-S.10^{kt})$ where Y=the percentage of alcohol converted into ether and X=the percentage of free acid in the mixture at the end of time t. Tables giving the values of the constants m, h, r, k, and S for the various temperatures and concentrations of sulphuric acid and alcohol are appended. A comprehensive thermodynamic study of the conditions of the reaction enables results to be deduced which are in general agreement with practical experience of ether manufacture. A laboratory investigation of the nature of the vapour given off showed that with a fall in the acidity of the mixture the quantity of alcohol in equilibrium with it increases and the proportion of ether in the vapour falls. [Cf. *B.*, 1924, 313.] H. C. R.

Termolecular Gas Reactions. I. Mechanism of the Formation of Acetic Acid from Acetaldehyde and Oxygen. A. KISS and L. DEMÉNY (*Rec. trav. chim.*, 1924, **43**, 221—248).—The reaction between pure acetaldehyde and pure oxygen was examined by the method previously described (A., 1923, ii, 237), the theory developed by Trautz (A., 1918, ii, 151) being applied. If the formation of an intermediate compound, $CH_3 \cdot CHO,O_2$, is postulated: $CH_3 \cdot CHO + O_2 = CH_3 \cdot CHO,O_2$; $CH_3 \cdot CHO,O_2 + CH_3 \cdot CHO = 2CH_3 \cdot CO_2H$, the velocity constant passes through a maximum with lapse of time, which suggests catalytic action. The reaction was also studied in presence of water vapour. At 20°, a long period of induction (10 hours) set in; at 60—80°, the induction period was shorter than for the dry gases at the same temperatures. These results showed that the action was autocatalytic, the formation of the autocatalyst being accelerated by moisture. The experimental results did not indicate whether the catalysis was chemical or physical. The autocatalyst is probably acetic acid: $CH_3 \cdot CHO + CH_3 \cdot CO_2H \rightleftharpoons CH_3 \cdot CHO,CH_3 \cdot CO_2H$ (infinitely rapid); $CH_3 \cdot CHO,CH_3 \cdot CO_2H + O_2 = CH_3 \cdot CO_2H + CH_3 \cdot CHO,O_2$ (measurable speed). The formation of this intermediate compound was shown to be a true gas reaction of the second order, catalysed by acetic acid but uninfluenced by water. With increasing oxygen pressure, the reaction is retarded; excess of aldehyde accelerates it, which seems to point to the complex $CH_3 \cdot CHO,CH_3 \cdot CO_2H$ as the catalyst. Indifferent gases (nitrogen, carbon dioxide) exerted no influence, neither, apparently, did the surface of the containing vessel. The reaction was not sensitive to light. S. K. T.

Ammonium Oleate. M. MLODZIEJEVSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 471—478).—Ammonium oleate when gently heated with alcohol dissolves, and on cooling crystallises in the form of plates possessing double refraction. When it is heated more strongly and then allowed to cool, a fine emulsion possessing double refraction is formed. This is followed by the appearance of fluid crystals in the form of "puppets" and sometimes also liquid spherolites and oily strips. On further cooling, the liquid crystals disappear; an emulsion is temporarily formed which is then followed by the appearance of the solid crystals. The same changes can be studied repeatedly on a single microscopic slide. S. P. S.

Simple and Mixed Acid Anhydrides. W. AUTENRIETH and G. THOMAE (*Ber.*, 1924, **57**, [*B*], 423—437; cf. A., 1901, i, 185).—It is shown that it is not possible to prepare mixed aliphatic–aromatic or aromatic–aromatic anhydrides either by the action of acetic anhydride on aromatic acids or by the action of the acid chloride on the sodium salt of another acid. The reaction given in Beilstein's "Handbuch" (3 *Aufl.*, **1**, 461): $(C_2H_3O)_2O + 2C_2H_5 \cdot OH = 2C_2H_3O_2 \cdot C_2H_5 + H_2O$, is shown to be incorrect, as in all cases examined 1 mol. of anhydride yielded only 1 mol. of ester and 1 mol. of free acid.

Ammonia, phenylhydrazine, and aniline react with aromatic anhydrides to give 1 mol. of free acid and 1 mol. of the acid amide, anilide, or hydrazide. Hydrazine hydrate reacts with *p*-toluic anhydride to give *s*-di-*p*-toluoylhydrazine, whilst a 50% aqueous solution of the base yields the monoacyl derivative,

$$C_6H_4Me \cdot CO \cdot NH \cdot NH_2.$$

p-Bromobenzoic anhydride yields only p-*bromobenzoylhydrazine*, m. p. 167°. The following anhydrides were prepared by the action of acetic anhydride on the requisite acid: stearic anhydride, m. p. 70—71°; palmitic anhydride, m. p. 62—63°; phenylacetic anhydride, prisms, m. p. 71—72°; *o*-toluic anhydride, m. p. 38—39°; m-*toluic anhydride*, prisms, m. p. 70—71°; *p*-toluic anhydride, leaflets, m. p. 95°; *p*-bromobenzoic anhydride, white plates, m. p. 218°; m-*nitrobenzoic anhydride*, prisms, m. p. 159—160°; p-*ethoxybenzoic anhydride*, m. p. 108° (which yields with aniline p-*ethoxybenzanilide*, m. p. 169°). The following new compounds are also noted: *Phenyl phenylacetate* (from phenylacetic anhydride and phenol), prisms, m. p. 42°. p-*Tolyl phenylacetate*, prisms, m. p. 75—76°. p-*Tolyl* p-*toluate* (from *p*-toluic anhydride and *p*-cresol), plates, m. p. 91—92°. F. A. M.

The Influence of Constitution on the Catalytic Hydrolysis of Esters by Acids. G. BERGER (*Rec. trav. chim.*, 1924, **43**, 163—177).—The rate of hydrolysis of about twenty esters of monobasic fatty acids and of substituted acetic and benzoic acids was studied. The catalyst used was *N*/10-hydrochloric acid and the medium of hydrolysis a mixture of alcohol and water containing 42·34% of alcohol. Experiments were carried out at different temperatures owing to the variation in ease of hydrolysis shown by the esters, and in calculating the reaction-velocity the presence of ethyl alcohol as solvent was recognised as a factor in the case of ethyl esters. The author draws the conclusions that the acceleration of hydrolysis brought about by hydrogen ions decreases with the strength of the ester acid (cf. Olivier and Berger, A., 1923, ii, 144) and, in the case of esters with negative alcoholic groups, *i.e.*, where the alcoholic constituent possesses a somewhat acid character, the acceleration is small. In the case of methyl and ethyl esters of the same acid, the difference in reaction velocity is not constant but decreases with the acidity of the ester. The accelerated action in the case of an ester of the type $R'\cdot CO_2R''$ is thus conditioned by both the R′ and R″ groups, and these groups appear to be of equal importance and strength in their influence on hydrolysis from both the qualitative and quantitative points of view. H. J. E.

Monocarboxylic Acids derived from Sugars. II. Methylation of Tetramethyl-gluconic Acid. J. PRYDE (*J. Chem. Soc.*, 1924, **125**, 520—522).—Tetramethyl-gluconolactone, treated with one molecular proportion of water, and then with methyl iodide and silver oxide at 40°, yields *methyl tetramethyl-gluconate*, $OMe\cdot CH_2\cdot CH(OMe)\cdot CH(OH)\cdot[CH(OMe)]_2\cdot CO_2Me$, a neutral, mobile oil, n_D^{15} 1·4480. On subjecting this to five successive methylations, *methyl pentamethyl-gluconate* was obtained as a neutral, colourless, limpid, very mobile oil, b. p. 100°/1·0 mm., n_D^{15} 1·4412, $[\alpha]_{5461}$ +42·7° in alcohol, and +24·9° in water, falling to +21·9° in 4 months. F. G. W.

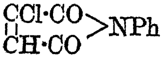
Oils in the Chaulmoogra Group. G. A. PERKINS and A. O. CRUZ (*Philippine J. Sci.*, 1923, **23**, 543—569).—The oils from the seeds of the following species were examined: *Gynocardia odorata, Hydnocarpus alcalæ, H. anthelminthica, H. Hutchinsonii, H. subfalcata, H. venenata, H. Wightiana, H. Woodii, Pangium edule,* and *Taraktogenos Kurzii.* The data obtained show a close similarity between the true chaulmoogra oil (from *Taraktogenos Kurzii*) and all the *Hydnocarpus* oils investigated. The oil from *Hydnocarpus alcalæ* is distinguished by its very high content of chaulmoogric acid. It contains little or no hydnocarpic acid. The other *Hydnocarpus* oils, like chaulmoogra oil, may each be separated by the distillation of the ethyl esters into fractions, one of which contains the acids with 16 carbon atoms and the other those with 18 carbon atoms. The former fractions of each oil contain hydnocarpic acid and an unknown acid or acids which cannot be completely separated from the hydnocarpic acid by one recrystallisation from 80% alcohol. This unknown acid portion has a lower optical activity than hydnocarpic acid. The latter fractions (acids with 18 carbon atoms) contain chaulmoogric acid, which can be separated more readily than hydnocarpic acid. A more highly unsaturated portion is left in the case of many samples when the chaulmoogric acid is crystallised out. Previous results placing *Gynocardia odorata* outside the chaulmoogra group were confirmed. *Pangium edule* seeds appear to contain no chaulmoogric or hydnocarpic acids. H. C. R.

Compounds Developed in Rancid Fats, with Observations on the Mechanism of their Formation. W. C. POWICK (*J. Agric. Res.*, 1923, **26**, 323—362).—A large number of possible products of rancidity in fats have been examined. It is suggested that nonaldehyde is in part responsible for the odour of rancid fats. The glyceryl radical and the unsaponifiable portion of fats appeared to have no part in the phenomena of rancidity, which may be reproduced by the oxidation of oleic acid. The colour developed in the Kreis test for rancidity was spectroscopically identical with that obtained by applying the test to a mixture of acraldehyde and hydrogen peroxide, and the essential compound appeared to be epihydrin aldehyde. Whilst this compound did not occur in rancid fats, a derivative, probably the acetal, is suggested as being the parent substance which is decomposed on the addition of hydrochloric acid in the Kreis test. A number of substances give a red coloration with phloroglucinol–hydrochloric acid, and spectroscopic examination is necessary to obtain positive evidence of rancidity. A possible mechanism for the formation of epihydrin aldehyde or its parent substance from fats is described. A. G. P.

Reactivity of Iodine towards Fats. III. Production of Acidity in the Reaction and the Mechanism of its Formation. B. M. MARGOSCHES and W. HINNER (*Chem. Umschau*, 1924, **31**, 41—45).—Acids are produced in the reaction between fats or unsaturated fatty acids and iodine solutions, the quantity varying with the solvent used for the iodine. Brown iodine solutions obtained with aqueous solvents or solvents miscible with water, from which an amount of iodine is absorbed by the fat which almost corresponds with its iodine value (Hübl), give a large amount of acid, corresponding with about half the iodine absorbed. Solutions of iodine in carbon tetrachloride, however, produce no acid in their action on fats, and other violet iodine solutions (in benzene, chlorinated ethylenes, and chloroform) give varying but comparatively small amounts of acid when they react on fats. In the action of aqueous and alcoholic iodine solutions on fats, an additive product of hypoiodous acid and the unsaturated molecule is formed, and not a simple iodine additive product as commonly supposed. This view is supported by the qualitative and quantitative production of acid. The action is analogous to Wijs' explanation of the action of his iodine monochloride solution on unsaturated linkings. The iodine from violet iodine solutions is mainly absorbed by unsaturated fats as such, but the reaction does not by any means proceed to completion. In the case of brown iodine solutions, the active mass of the hydrogen iodide formed during the reaction, or added to the solution, opposes itself to the complete addition of hypoiodous acid to the unsaturated linkings, and so reduces the absorption of iodine. H. C. R.

Oxidation of Lumbang and Linseed Oils and of the Principal Compounds in Lumbang Oil. A. P. West and A. I. de Leon (*Philippine J. Sci.*, 1924, **24**, 123—140).—When lumbang and linseed oils are blown under the same conditions at 75°, the percentage of apparent oxygen absorption, volatile products evolved, and total oxygen absorption in the early stages of oxidation are greater for lumbang than for linseed oil. As the oxidation process continues, the velocity of oxygen absorption increases more rapidly for linseed than for lumbang oil until after 100 hours the percentage of total oxygen absorption of linseed is greater than that of lumbang oil. Data giving the total percentage of oxygen absorption per hour during definite periods of time for these two oils indicate that for about the first 30 hours lumbang oil absorbs oxygen much more rapidly than does linseed oil. After 30 hours of oxidation, the rate of absorption of oxygen by lumbang oil gradually decreases, whilst the corresponding rate for linseed oil considerably increases. Both oils have about the same absorption velocity for oxygen for the period of oxidation extending from 30 to 40 hours. In the case of linseed oil, the velocity of oxygen absorption increases continually up to a period of 100 hours, beyond which the oxidation experiments were not continued. Both linseed and lumbang oils contain linolenic, linolic, and oleic glycerides, and also saturated glycerides. Linseed oil contains a much larger percentage of linolenic glycerides and of saturated glycerides than does lumbang oil. Possibly autocatalysts are formed in both these oils during oxidation and tend to accelerate the velocity of oxygen absorption, whilst the saturated glycerides present tend to retard the velocity of absorption. Constants of samples of lumbang and linseed oils blown for various periods of time at 75° were determined. Both oils gave very similar results. The surface tensions and refractive indices of both oils increased slightly on oxidation, whilst the iodine values decreased considerably. Samples of lumbang oil oxidised for various periods of time were analysed. The percentage of oxidised glycerides increased, whilst the percentage of unoxidised unsaturated glycerides decreased. The linolenic glycerides of lumbang oil were oxidised more readily than the linolic and the linolic more readily than the oleic glycerides. H. C. R.

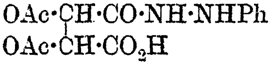
Quantitative Reduction by Hydriodic Acid of Halogenated Malonyl Derivatives. III. Mechanism of the Reaction. R. W. West (*J. Chem. Soc.*, 1924, **125**, 710—721).—The reaction between α-bromomalonyldimethylamide and hydriodic acid is bimolecular, and is probably indicated by the scheme $\cdot CO\cdot CHBr\cdot \longrightarrow \cdot C(OH){:}Br\cdot \longrightarrow \cdot CI(OH)\cdot CHBr\cdot \longrightarrow \cdot C(OH){:}CH + IBr$ (cf. Meyer, A., 1911, i, 350). The rate of reaction between hydriodic acid and αα′-dibromo-, αα′-chlorobromo-, and α-bromo-α′-alkylmalondimethylamides is independent of the concentration of the potassium iodide, but varies with that of the acid present, indicating that the primary (slow) reaction is the hydrolysis $:CXBr + H_2O = :CXH + HOBr$, which is followed by the instantaneous reduction of the hypobromous acid. The rate of reduction of the α-bromo-α′-alkylmalondimethylamides decreases in the order *iso*butyl (methyl), *n*-propyl, *iso*propyl, *n*-butyl, ethyl, which is identical with that for the rates of formation of the methylamides from the corresponding ethyl α-alkylmalonates. The effect is to be ascribed to steric hindrance rather than to polarity. The following α-alkylmalondimethylamides are obtained by heating the corresponding α-alkylmalonic ethyl esters with alcoholic monomethylamine at 100—140°: α-*methyl-*, colourless plates, m. p. 154°; α-*ethyl-*, small needles, m. p. 176°; α-n-*propyl-*, thin needles, m. p. 171°; α-iso*propyl-*, colourless needles, m. p. 167°; α-n-*butyl-*, colourless needles, m. p. 177°, and α-iso*butyl-malonodimethylamide*, thin needles, m. p. 163°. α-*Bromo-*α′-*methylmalonodimethylamide*, colourless needles, m. p. 114°, was prepared by brominating the above methyl derivative in chloroform, the following by brominating the corresponding α-alkylmalonodimethylamides in glacial acetic acid, all as colourless needles: α-*bromo-*α′-*ethyl-*, m. p. 136°; α-*bromo-*α′-n-*propyl-*, m. p. 106°; α-*bromo-*α′-iso*propyl-*, m. p. 101°; α-*bromo-*α′-n-*butyl-*, m. p. 89°, and α-*bromo-*α′-iso*butyl-malonodimethylamide*, m. p. 111°. F. G. W.

Action of Diacetyltartaric Anhydride and Chlorofumaryl Chloride on Aromatic Amines and Hydrazines. F. D. Chattaway and G. D. Parkes (*J. Chem. Soc.*, 1924, **125**, 464—470).—Phenyliminosuccinanil (cf. T., 1923, **123**, 663) is obtained by the action of aniline on chlorofumaranilide at 150°. *Chloromaleinanil*,  $\left.\begin{matrix} CCl\cdot CO \\ \| \\ CH\cdot CO \end{matrix}\right> NPh$, small, colourless needles, m. p. 170°, is formed on heating the aniline salt of chloromaleic or chlorofumaric acid at 170—180°, and yields phenyliminosuccinanil on heating with aniline. *Chloromalein-*p-*chloroanil*, minute, glistening, irregular plates, m. p. 175°, and *chloromalein-*p-*bromoanil*, microcrystalline powder, m. p. 190°, are obtained similarly. *Chlorofumarodiamide*,

$CONH_2\cdot CCl\colon CH\cdot CONH_2$, needles, m. p. 187°, *chlorofumaro-dimethylamide*, minute, colourless needles, m. p. 173°; *-di-p-chloroanilide*, clusters of pale yellow needles, m. p. 223°; and *-di-p-bromoanilide*, minute, faintly yellow needles, m. p. 236°, are obtained by the action of chlorofumaryl chloride on ammonia and the corresponding amines, respectively. The di-*p*-bromoanilide is also obtained by the action of bromine in glacial acetic acid on chlorofumarodianilide.

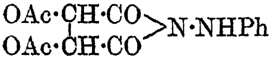
Aqueous potassium hydroxide hydrolyses phenyliminosuccinanil with formation of β-anilinoacrylic acid, whilst in alcohol the products are aniline, potassium oxalate, and potassium acetate.

Phenylhydrazine diacetyltartrate, a white, microcrystalline powder, melts partly at about 70° with loss of water and formation of *diacetyltartarophenylhydrazido-acid* (I), m. p. 168°, with formation of *α-diacetyltartarophenylhydrazide* (II), small, faintly yellow needles,



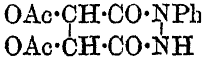
$$\begin{array}{l} OAc\cdot CH\cdot CO\cdot NH\cdot NHPh \\ OAc\cdot CH\cdot CO_2H \end{array}$$

(I.)



$$\left.\begin{array}{l} OAc\cdot CH\cdot CO \\ OAc\cdot CH\cdot CO \end{array}\right> N\cdot NHPh$$

(II.)



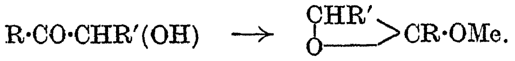
$$\begin{array}{l} OAc\cdot CH\cdot CO\cdot NPh \\ OAc\cdot CH\cdot CO\cdot NH \end{array}$$

(III.)

m. p. 156°, and this, on warming with sodium ethoxide in alcohol, is converted into β-*diacetyltartarophenylhydrazide* (III), minute, colourless, irregular plates, m. p. 256°. The action of excess of phenylhydrazine on diacetyltartaric anhydride, or on the above α-hydrazide, affords tartarodiphenylhydrazide (T., 1903, **83**, 1349) and acetylphenylhydrazine. F. G. W.

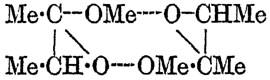
Formals of Primary Alcohols. M. GHYSELS (*Bull. Soc. chim. Belg.*, 1924, **33**, 57—78).—Formals have been prepared by a direct distillation method from methyl, ethyl, *n*-propyl, *n*-butyl, *iso*butyl, and *n*-amyl alcohols. A non-volatile catalyst such as sulphuric acid or toluene-*p*-sulphonic acid is used which is eliminated immediately by the distillation. High yields of practically pure formals can be obtained in a single operation except in the cases of methylformal and ethylformal. Methylformal forms with the excess of alcohol an azeotropic mixture containing 92·15% of formal. Ethylformal gives a ternary azeotropic mixture with the excess of alcohol and the water produced in the reaction, from which it is separated by the addition of carbon disulphide; after separation of the aqueous layer and removal of the carbon disulphide, the ethylformal is obtained practically pure. *n*-Propylformal also yields a ternary azeotropic mixture with the excess of alcohol and water. All the formals prepared give binary azeotropic mixtures with water. The boiling points and approximate composition of these mixtures are given. R. B.

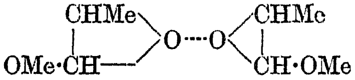
Glucosidic Acetals derived from Simple α- or β-Hydroxyketones and their Polymerisation. M. BERGMANN and S. LUDEWIG (*Annalen*, 1924, **436**, 173—183; cf. Bergmann and Miekeley, A., 1921, i, 763; Fischer, A., 1895, i, 437).—The formation of glucosidic compounds from α- or β-hydroxy-aldehydes or -ketones has not previously been observed. The authors have shown that simple α-hydroxyketones, such as acetol, acetoin, and benzoylcarbinol, yield glucosidic *cyclo*acetals on treatment with methyl alcohol and hydrogen chloride, according to the scheme



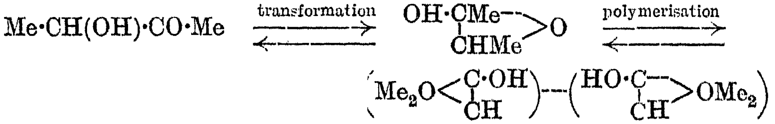
$$R\cdot CO\cdot CHR'(OH) \longrightarrow \begin{matrix} CHR' \\ O\text{———} \end{matrix}\!\!>CR\cdot OMe.$$

These *cyclo*acetals polymerise easily, being bimolecular in solution and in the vapour phases at low pressures and temperatures; when strongly heated, they dissociate, but on cooling the bimolecular form is again obtained as crystals. This phenomenon is a property of an αβ-oxygen bridge in glucosides, but the three cases mentioned are peculiar, as in the gaseous state they are easily dissociated. The acetals of acetoin and glycollaldehyde are bimolecular over a comparatively wide range of temperature, whereas acetol*cyclo*acetal is dissociated at 100° under a pressure of a few millimetres. The derivatives of benzoylcarbinol cannot be examined owing to their high melting points. The following formulæ are suggested for dimeric acetoin*cyclo*acetal.





It is known that α-hydroxy-aldehydes and -ketones themselves polymerise to bimolecular forms, acetoin being an example. Refractometric measurements indicate that the unimolecular liquid form of acetoin possesses an alicyclic hydroxy-carbonyl structure. The change to the bimolecular crystalline form and the slow reverse change (at the ordinary temperature) indicate some structural alteration for which the following scheme is suggested:



Acetoin, b. p. 140—144°, d_4^{17} 0·9972, $n_D^{17\cdot3}$ 1·4190, is best prepared from γ-bromobutan-β-one by warming with an excess of potassium formate in dry methyl alcohol or with water and freshly precipitated calcium carbonate or potassium hydrogen carbonate. It is converted by acetic anhydride and pyridine into the acetate, b. p. 169—173°, $d_4^{16\cdot5}$ 1·038, $n_D^{16\cdot5}$ 1·4157.

Acetoin may be polymerised by the action of granulated zinc at —15° (cf. Diels and Stephan, A., 1907, i, 1000), when colourless crystals slowly separate, m. p. 83° (cf. von Pechmann and Dahl, A., 1890, 1234). Vapour density determinations in all cases were made by the method of Bleyer and Kohn, whence M=91 (req.=88) at 140°/2 mm. *Methyl*cyclo*acetal* was prepared from acetoin by the action of 1% methyl-alcoholic hydrogen chloride at 0°; bisacetoin may be employed (m. p. 73—73·5°, b. p. 196—198°/745 mm.). In phenol solution, it is bimolecular and also at 80°/0·8 mm., but at higher temperatures the vapour dissociates and is unimolecular at 140°/2 mm.

Acetol methyl*cyclo*acetal (m. p. 127°), prepared from acetol by means of methyl-alcoholic hydrogen chloride, at 100°/10 mm. is partly bimolecular, but at 140°/1·5 mm. it is unimolecular.

Ethylglycoloside (cf. Bergmann and Miekeley, *loc. cit.*) is bimolecular at 140°/8 mm., and unimolecular at 180°/10 mm.

The methyl*cyclo*acetal of benzoylcarbinol, m. p. 192°, was unimolecular at 200°, but at higher temperatures some secondary changes took place which interfered with the accuracy of the measurements. A. E. C.

Isomerism of Thioaldehydes. E. FROMM and M. SOFFNER (*Ber.*, 1924, **57**, [*B*], 371—373).—A reply to Hinsberg (A., 1923, i, 1056; cf. Fromm and Schultis, A., 1923, i, 580).—The crude product (m. p. 216°) of the action of hydrogen sulphide on formaldehyde, whether freshly prepared or preserved during several months, loses hydrogen sulphide when treated with lead oxide and sodium hydroxide. It is converted into the substance, m. p. 247° (Hinsberg's β-trithioformaldehyde), not only by hydriodic acid, but also by concentrated hydrochloric acid; the change is therefore due to transformation and not to reduction. The sulphoxides derived from trithioformaldehyde, m. p. 216°, and from the substance, m. p. 247°, are probably identical; their solubilities are the same, and they yield the same product when treated with concentrated hydriodic acid.

The properties of the compound formed from hydrogen sulphide and formaldehyde appear to be in harmony with the formula $SH\cdot CH_2\cdot S\cdot CH_2\cdot S \ldots\ldots CH_2\cdot S\cdot CH_2\cdot SH$; the length of the chain cannot be determined, since there is no available method for the examination of the molecular weight of the compound. Oxidation of trithioformaldehyde or of the polymeric thioaldehyde, m. p. 247°, by hydrogen peroxide in acetic acid solution does not afford much insight into their constitution, since it is very probable that either compound is resolved into monomeric thioformaldehyde in the initial stages of the change.

α-Trithioformaldehyde, m. p. 216°, is the only compound of the group to which a definite molecular weight can be assigned. The degree of polymerisation of the product, m. p. 247°, cannot be ascertained, and it is purely arbitrary to regard it as a trimeride. H. W.

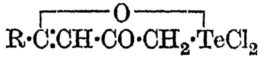
Formation of Acetone from Acetates. E. HÄGGLUND and E. O. HEDMAN (*J. pr. Chem.*, 1924, [ii], **107**, 50—64).—Dry distillation of sodium acetate at 400° in a current of steam gives nearly as high a yield of acetone as the distillation of calcium acetate; when inert gases such as nitrogen are used in place of steam, the yield of acetone is not raised in this way. Mixing the sodium acetate with calcium oxide or carbonate or sodium carbonate raises the yield of acetone considerably, and also accelerates the reaction, acetone formation being practically complete in the first hour instead of in 3—4 hours. This accelerating action was also observed in an atmosphere of nitrogen. Rather more carbon monoxide and less carbon dioxide were produced than in the distillation of calcium acetate. Methane was only produced in quantity when sodium hydroxide was added to the sodium acetate; in this case very little acetone was produced. R. B.

Density and Viscosity of Acetone at Low Temperatures. E. H. Archibald and W. Ure (*J. Chem. Soc.*, 1924, **125**, 726—731).—The following values were obtained for the density of acetone at the temperatures given: 0·0°, 0·8140; —10·0°, 0·8251; —20·0°, 0·8370; —30·0°, 0·8473; —40·0°, 0·8575; —50·0°, 0·8777; —70·0°, 0·8884; —80·0°, 0·9002; and —90·0°, 0·9117. Corresponding viscosities (absolute units) are: 0°, 0·00389; —10·6°, 0·00451; —20·4°, 0·00517; —30·3°, 0·00613; —40·0°, 0·00713; —49·9°, 0·00818; —59·7°, 0·00981; —69·7°, 0·01200; —79·7°, 0·01505; and —89·7°, 0·02051. The large increase in viscosity–temperature coefficient may account for the large conductivity–temperature coefficients found for solutions of organic substances in the liquid halogen hydrides. F. G. W.

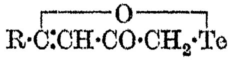
Interaction of Tellurium Tetrachloride and the Higher β-Diketones. I. G. T. Morgan and H. D. K. Drew (*J. Chem. Soc.*, 1924, **125**, 731—754).—The course of the reaction between tellurium tetrachloride and β-diketones, in chloroform or benzene, is determined by the complexity of the carbon chain of the diketone. If the solvent contains alcohol, the latter may enter into the reaction. The tellurium β-diketones, obtained by reducing the tellurium β-diketone dichlorides with potassium metabisulphite, are powerful bactericides (*Biochem. J.*, 1924, **18**, 190).

[With C. R. Porter.]—*n*-Butyrylacetone yields, in pure chloroform, *tellurium* n-*butyrylacetone dichloride* (I), transparent, colourless prisms, m. p. 153—154° after darkening at 144°; in presence of alcohol, *tellurium* O-*ethyl*-n-*butyrylacetone trichloride* (III), golden-yellow needles, m. p. 105·5—106·5° (decomp.), is also formed.

(I.)



$R\cdot C\colon CH\cdot CO\cdot CH_2\cdot TeCl_2$ (ring closed through O)



$R\cdot C\colon CH\cdot CO\cdot CH_2\cdot Te$ (ring closed through O)

(II.)

$C_3H_7\cdot C(OEt)\colon CH\cdot CO\cdot CH_2\cdot TeCl_3$ (III.)

$C_6H_{13}\cdot CO\cdot CH\colon C(OH)\cdot CH_2\cdot TeCl_3$ (IV.)

Tellurium n-*butyrylacetone*, $C_7H_{10}O_2Te$ (II), forms yellow needles, m. p. 110—112°. *n*-Heptoylacetone yields *tellurium* n-*heptoylacetone dichloride* (see I), nacreous, compact, or acicular prisms, m. p. 87°, and *tellurium* n-*heptoylacetone trichloride* (IV), colourless, nacreous, six-sided plates, m. p. 117° (decomp.). *Tellurium* n-*heptoylacetone*, $C_{10}H_{16}O_2Te$ (see II), forms yellow needles or golden-yellow scales, m. p. 86°, and shows residual acidity. The trichloride is not converted into the cyclic dichloride on boiling with pure chloroform, and addition of anhydrous aluminium chloride led to the formation of a crystalline aluminium derivative.

[With I. Ackerman.]—Dipropionylmethane yields *tellurium dipropionylmethane dichloride*, $C_7H_{10}O_2Cl_2Te$, thin, colourless, six-sided plates (from acetone or benzene) darkening at 157°, and intumescing at 162°, or glistening prisms (from methyl alcohol), darkening at 150° and intumescing at 170° (cf. T., 1921, **119**, 616), and *tellurium* O-*ethylpropionylmethane trichloride*, $C_9H_{15}O_2Cl_3Te$, transparent, lemon-yellow prisms, m. p. 110—111° (decomp.). *Tellurium dipropionylmethane*, $C_7H_{10}O_2Te$, forms very tough, golden-yellow needles, m. p. 151° (decomp.), sublimes at 110° under reduced pressure, and shows no enolic reactions.

Tellurium propionyl-n-*butyrylmethane dichloride*, $C_8H_{12}O_2Cl_2Te$, forms silvery flakes, darkening at 150°, m. p. 156° (decomp.). *Tellurium propionyl*-n-*butyrylmethane*, $C_8H_{12}O_2Te$, forms yellow needles, m. p. 101—102° (decomp.). *iso*Butyrylacetone (b. p. 163°/752·5 mm.; *copper* salt, light blue, voluminous, crystalline powder, m. p. 167—168°) yields *tellurium* O-*ethyl*iso*butyrylacetone trichloride*, $C_9H_{15}O_2Cl_3Te$, pale yellow flakes or needles, m. p. 103° (decomp.). *iso*Valerylacetone (b. p. 183°/741 mm.; copper salt, m. p. 154°) yields *tellurium bis*iso*valerylacetone dichloride*,

$$C_{16}H_{26}O_4Cl_2Te,$$

transparent, colourless, acicular prisms, or nacreous leaflets, m. p. 97—98° (decomp.), and *tellurium* O-*ethyl*iso*valerylacetone trichloride*, small, compact, lemon-yellow, gem-like crystals, changing at 88° to a yellow glass having m. p. 101—102° (decomp.). *γ-Methylpropionylacetone* [*copper* salt, dark olive-green crystals, m. p. 174—176° (decomp.), or greenish-grey needles, m. p. 175—177° (decomp.)], yields *tellurium γ-methylpropionylacetone dichloride*, colourless, glistening prisms, m. p. 166—167° (decomp.) after sintering at 164°, which is reduced to the neutral *tellurium γ-methylpropionylacetone*, long, soft, pale golden needles, or elongated prisms, m. p. 125—126° (decomp.), subliming at 100° in a vacuum. *γ-Ethyl*-n-*butyrylacetone*, colourless, fragrant oil, b. p. 101—102°/9 mm. [*copper* salt, m. p. 166° (decomp.)], yields *tellurium γ-ethyl*-n-*butyrylacetone dichloride*, nacreous rosettes of colourless, prismatic needles, m. p. 140° (decomp.). *Tellurium γ-ethyl*-n-*butyrylacetone*,

$$C_9H_{14}O_2Te,$$

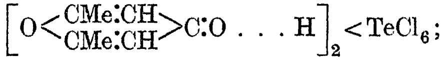
forms yellow needles, sintering at 110°, m. p. 113°, and is non-enolic.

Dipropionylethylmethane, $Et\cdot CH(CO\cdot Et)_2$, forms a colourless oil with a pleasant, slightly peppery odour, b. p. 105—106°/13 mm., 202—203°/744 mm. [*copper* salt, grey, microcrystals (from alcohol), m. p. 178—180°, or silver-grey needles (from benzene), m. p. 174—176°]. *Tellurium dipropionylethylmethane dichloride* forms colourless, transparent, six-sided prisms, darkening from 172°, m. p. 182° (decomp.), and is reduced to *tellurium dipropionylethylmethane*, tough, golden needles, m. p. 137—138° (decomp.), subliming at 110° in a vacuum. *Tellurium γγ-diethylacetylacetone dichloride* forms colourless, nacreous flakes or prisms, softening at 177°, m. p. 178—180°. *Tellurium γγ-diethylacetylacetone* forms brittle, yellow, acicular needles, or needles with characteristically serrated edges, m. p. 85—86°, and has no residual acidity.

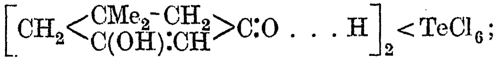
Diacetylacetone yields a mixture of *dimethylpyrone tellurichloride* (V), spear-like aggregates of golden-yellow needles, and the *oxy-*

chloride $[(C_7H_8O_2)H]_2TeOCl_4$, colourless crystals, m. p. 115°. Tetraacetylethane yields a *substance* crystallising in pale golden, six-sided plates or needles, blackening at 135°, which is hydrolysed

(V.)



$$\left[\mathrm{O}{<}\begin{smallmatrix}\mathrm{CMe{:}CH}\\ \mathrm{CMe{:}CH}\end{smallmatrix}{>}\mathrm{C{:}O}\ .\ .\ .\ \mathrm{H}\right]_2{<}\mathrm{TeCl_6};$$



$$\left[\mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{CMe_2{-}CH_2}\\ \mathrm{C(OH){:}CH}\end{smallmatrix}{>}\mathrm{C{:}O}\ .\ .\ .\ \mathrm{H}\right]_2{<}\mathrm{TeCl_6};$$

(VI.)

with formation of 3 : 4-diacetyl-2 : 5-dimethylfuran, of which it is probably the tellurichloride. Dimethyldihydroresorcinol affords *dimethyldihydroresorcinol tellurichloride* (VI), large, transparent, pale yellow prisms, resinifying at 130°, m. p. 160—165° (decomp.). Ethyl acetoacetate yields *tellurium ethyl* O-*ethylacetoacetate trichloride* (*tellurium ethyl* β-*ethoxycrotonate trichloride*),

$$\mathrm{CO_2Et{\cdot}CH{:}C(OEt){\cdot}CH_2{\cdot}TeCl_3},$$

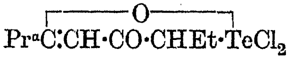
colourless plates, softening at 88°, m. p. 90—92° (decomp. 140°). Definite products were not obtained by condensing tellurium tetrachloride with ethyl malonate, 3-allylacetylacetone, acetylmesityl oxide, acetylcamphor, ω-phenylacetylacetone, benzylidenebisacetylacetone (non-enolic and dienolic forms) and 2-acetyl*cyclo*hexanone). The benzeneazo-β-diketones yield bright yellow, stable compounds containing tellurium and halogen. F. G. W.

Interaction of Tellurium Tetrachloride and the Higher β-Diketones. II. G. T. MORGAN and R. W. THOMASON (*J. Chem. Soc.*, 1924, **125**, 754—759).—*Dibutyrylmethane*,

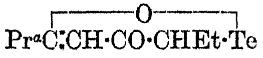
$$\mathrm{CH_2(CO{\cdot}C_3H_7)_2},$$

is obtained as a fragrant, colourless liquid, b. p. 204—205°, by the condensation of methyl propyl ketone with *n*-butyl *n*-butyrate or (in better yield) with ethyl *n*-butyrate. It forms a blue *copper* salt, m. p. 156°, and condenses with *p*-nitrophenylhydrazine to form 1-p-*nitrophenyl*-3 : 5-*di*-n-*propylpyrazole*, $C_{15}H_{19}O_2N_3$, yellowish-brown needles, m. p. 53°. It condenses with tellurium tetrachloride in chloroform with formation of *tellurium dibutyrylmethane dichloride* (I), vitreous needles (from methyl alcohol), m. p. 148°, or colourless needles (from alcohol or chloroform–petroleum), m. p. 120—139° or 138—139°, and *tellurium dibutyrylmethane trichloride*, $\mathrm{Pr^{\alpha}CO{\cdot}CH{:}C(OH){\cdot}CHEt{\cdot}TeCl_3}$ or $\mathrm{Pr^{\alpha}C(OH){:}CH{\cdot}CO{\cdot}CHEt{\cdot}TeCl_3}$, large, tabular crystals, m. p. 87—88°, with blackening. Both forms of the dichloride are reduced, with alkali hydrogen sulphite, to *tellurium dibutyrylmethane* (II), golden-yellow needles, m. p. 97°.

(I.)



$$\mathrm{Pr^{\alpha}\overbrace{C{:}CH{\cdot}CO{\cdot}CHEt{\cdot}Te}^{O}Cl_2}$$



$$\mathrm{Pr^{\alpha}\overbrace{C{:}CH{\cdot}CO{\cdot}CHEt{\cdot}Te}^{O}}$$

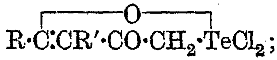
(II.)

γ-*Ethylpropionylacetone*, $C_2H_5{\cdot}CO{\cdot}CHEt{\cdot}CO{\cdot}CH_3$, obtained by the action of ethyl iodide on sodium propionylacetone, forms a fragrant oil, b. p. 192—193°/755 mm. (*copper* salt, m. p. 176°). *Tellurium* γ-*ethylpropionylacetone dichloride*, $C_8H_{12}O_2Cl_2Te$, acicular prisms, m. p. 167° (decomp.), and *tellurium* γ-*ethylpropionylacetone*, $C_8H_{12}O_2Te$, pale yellow needles, m. p. 109°, are described.

γ-n-*Propylacetylacetone* was obtained as a fragrant oil, b. p.

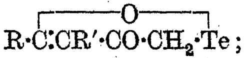
191—192°/745 mm. (*copper* salt, m. p. 215°), by the action of *n*-propyl iodide on sodium acetylacetone at 180° under pressure (cf. T., 1920, **117**, 780). *Tellurium* γ-n-*propylacetylacetone dichloride*, $C_8H_{12}O_2Cl_2Te$, forms colourless, acicular prisms, m. p. (indefinite) 180°. *Tellurium* γ-n-*propylacetylacetone*, $C_8H_{12}O_2Te$, forms pale yellow needles, m. p. 106—107°. γ-iso*Propylacetylacetone*, prepared similarly to the *n*-propyl derivative, b. p. 182—183°/745 mm., has an odour of dry hay. It does not form a copper salt, and gives no coloration with ferric chloride. *Tellurium* γ-iso*propylacetylacetone dichloride* forms lustrous, colourless, acicular prisms, blackening indefinitely at about 150°. *Tellurium* γ-iso*propylacetylacetone* forms yellow needles, m. p. 152—153°. F. G. W.

Interaction of Tellurium Tetrachloride and the Higher β-Diketones. III. G. T. Morgan and E. Holmes (*J. Chem. Soc.*, 1924, **125**, 760—765).—The isolation of the condensation products of tellurium tetrachloride and the β-diketones is rendered more difficult, as the series is ascended, by their increasing fusibility and solubility in organic media. n-*Valerylacetone*, a pungent oil, b. p. 194° (blue *copper* salt, m. p. 143°), is converted by tellurium tetrachloride into *tellurium* n-*valerylacetone dichloride*, $C_8H_{12}O_2Cl_2Te$ ($R=n\text{-}C_4H_9$, $R'=H$, in formula I), colourless needles, m. p. 125°; this is reduced by potassium metabisulphite to *tellurium* n-*valerylacetone*, $C_8H_{12}O_2Te$ (see II), yellow needles, m. p. 80°. *n*-Hexoylacetone (blue *copper* salt, m. p. 138°) gives *tellurium* n-*hexoylacetone dichloride* ($R=n\text{-}C_5H_{11}$, $R'=H$, in I), colourless needles, m. p. 102°. *Tellurium* n-*hexoylacetone* (see II) forms brilliant yellow needles, m. p. 86°.



$\overbrace{R\cdot C{:}CR'\cdot CO\cdot CH_2\cdot Te}^{O}Cl_2$;

(I.)



$\overbrace{R\cdot C{:}CR'\cdot CO\cdot CH_2\cdot Te}^{O}$;

(II.)

γ-n-*Butylacetylacetone*, b. p. 210—212°/750 mm. (grey *copper* salt, m. p. 186°) was prepared by the action of *n*-butyl iodide on sodium acetylacetone. *Tellurium* γ-n-*butylacetylacetone dichloride* ($R=CH_3$, $R'=n\text{-}C_4H_9$, in I), lustrous, colourless crystals, m. p. 155°, is reduced to *tellurium* γ-n-*butylacetylacetone* (see II), primrose-yellow needles, m. p. 129°. γ-n-*Butylpropionylacetylacetone*, similarly obtained from propionylacetone, has b. p. 223—224°/745 mm. (*copper* salt, grey needles, m. p. 156°). *Tellurium* γ-n-*butylpropionylacetone dichloride* ($R=C_2H_5$, $R'=n\text{-}C_4H_9$, in I), forms colourless leaflets, m. p. 103°. *Tellurium* γ-n-*butylpropionylacetone* (see II) forms golden-yellow needles, m. p. 93°. Methyl *n*-nonyl ketone was condensed with ethyl acetate and sodium to form n-*decoylacetone*, an oil with a sweet, penetrating odour, b. p. 276°/760 mm. (*copper* salt, pale blue needles, m. p. 114°). *Tellurium* n-*decoylacetone dichloride* ($R=n\text{-}C_9H_{19}$, $R'=H$, in I), forms grey crystals, m. p. 49°, and *tellurium* n-*decoylacetone* (see II), yellow needles, m. p. 64°. F. G. W.

Bactericidal Action of the Tellurium Derivatives of Aliphatic β-Diketones. II. G. T. Morgan, E. A. Cooper, and A. W. Burtt.—(See i, 591.)

Pentosans. VII. Fusion of Xylan with Potassium Hydroxide. E. HEUSER and J. ROTH (*J. pr. Chem.*, 1924, [ii], **107**, 1—6; cf. A., 1923, i, 1061, 1181).—Fusion of xylan with 10 parts of potassium hydroxide and an equal weight of water for ½ hour to 2 hours gives oxalic, acetic, and formic acids in amounts depending on the temperature. Oxalic acid is formed most readily at 220—250° (yield 53%), with some evolution of hydrogen. Below 200° much xylan remains unchanged. The yields of acetic acid and formic acid at 230—280° vary from 13—15% and 9—12%, respectively. The presence of succinic acid has been proved, but its amount could not be determined. Succinic acid is not formed in the fusion and subsequently decomposed, for this acid was recovered practically unchanged after fusion with potassium hydroxide. Traces of pyrocatechol and protocatechuic acid have been detected, but the presence of these and other aromatic substances is attributed to the presence of impurities in the xylan. The amount of formic acid produced leads to the conclusion that the oxalic acid results from decomposition of the formate, as in the fusion of cellulose, a conclusion which was confirmed by measuring the hydrogen evolved when the fusion was conducted in a stream of nitrogen. R. B.

Mutarotation of the Sugars. R. GILMOUR (*J. Chem. Soc.*, 1924, **125**, 705—706).—A question of priority (cf. Gilmour, P., 1909, **25**, 225; Baker, Ingold, and Thorpe, this vol., i, 262). F. G. W.

Chemical Effects of γ-Rays of Radium. A. SLOSSE (*Compt. rend. Soc. Biol.*, 1923, **89**, 96—98; from *Chem. Zentr.*, 1924, i, 33—34).—The effect of the radiations from radium bromide enclosed in a sealed tube and immersed in a solution of pure dextrose was to produce a small decrease in optical activity, attributed to a partial transformation of β- into γ-dextrose. The presence of formaldehyde was established; no other degradation products of dextrose were found. After subjection to radiation, the dextrose solution became much more readily oxidisable by potassium permanganate and sulphuric acid. G. W. R.

Glucose [Dextrose] from α- and β-Glucosides. H. COLIN and [MLLE.] A. CHAUDUN (*Compt. rend.*, 1924, **178**, 779—782).—The hydrolysis of α- and β-methyl-, of α- and β-ethyl-glucosides, and of salicin, has been followed polarimetrically and by copper titration. Salicin hydrolyses initially to give a glucose of low rotatory power (increasing with time) and is therefore a β-glucoside. E. E. T.

Acetone-sugars and their Derivatives. I. The Constitution of Glucosediacetone [Di*iso*propylidene-glucose] and a new Benzoylglucosemonoacetone. H. OHLE (*Ber.*, 1924, **57**, [*B*], 403—409).—The action of aniline hydrochloride on benzoylglucosediacetone (Fischer and Noth, A., 1918, i, 226) in boiling, absolute alcoholic solution leads to the formation of a second *benzoylglucosemonoacetone*, $CMe_2{:}C_6H_9O_5{\cdot}OBz$, $[\alpha]_D^{20}$ −26° in alcoholic solution, which could not be caused to crystallise. In so far as hydrolysis does not occur, it is stable towards dilute acids, but is rapidly converted by traces of alkali into the crystalline benzoylglucosemonoacetone of Fischer and Noth (*loc. cit.*). The constitution of the new derivative has not been established completely, but it is considered to be the primary product of the action from which Fischer's compound is obtained by isomerisation. Since Fischer, Pfähler, and Brauns (A., 1920, i, 840) have shown that the wandering of acyl groups occurs from the secondary to the primary alcoholic hydroxy group, it is assumed that the crystalline product is ζ-benzoylglucosemonoacetone. This hypothesis is supported by the observations that it is the sole isolable product of the action of benzoyl chloride on glucosemonoacetone in the presence of pyridine, and that both benzoylglucosemonoacetones are convertible into the same tribenzoylglucosemonoacetone, the experimental conditions being such that isomerisation is excluded.

Glucosemonoacetone reacts with acetone to form glucosediacetone as readily in the presence of anhydrous copper sulphate as in that of hydrogen chloride. A similarly ready reaction is observed in the cases of glycerol and of glyceryl α-benzoate.

It is suggested that the wandering of acyl and alkyl groups is more frequent than has been assumed previously in the chemistry of the sugars. The discordant results obtained by Irvine and Patterson (T., 1922, **121**, 2146) and by Levene and Meyer (A., 1923, i, 92) by the oxidation of methylglucosediacetone are probably attributable to this cause. H. W.

Crystallisation of Sucrose. J. A. KUCHARENKO (*Louisiana Planter*, 1923, **71**, 211—213, 231—232).—The concentration of supersaturated solutions of sucrose at the instant of crystallisation was determined at various temperatures; by the correlation of surface, S, and weight, P, in the equation $S^3 = kP^2$, the rate of crystallisation of solutions of various degrees of supersaturation could be accurately measured. The speed of crystallisation was found to vary directly with the degree of supersaturation and with the temperature employed. CHEMICAL ABSTRACTS.

The System Maltose–Water. J. GILLIS (*Rec. trav. chim.*, 1924, **43**, 135—143).—The author has studied the lowering of the melting point of ice for high concentrations of maltose both in pure water and in the presence of ammonia. The resulting curve is shown together with the solubility curve of maltose between 0° and 96·5°. From the latter, the inference is drawn that the monohydrate of β-maltose exists as the solid phase in equilibrium with the solution up to the neighbourhood of 100°. The solubility curve is compared with the curves of lactose (Gillis, A., 1921, i, 11) and of dextrose (Jackson and Silsbee, A., 1922, i, 986). H. J. E.

Acetobromomaltose. H. FISCHER and F. KÖGL (*Annalen*, 1924, **436**, 219—228; cf. E. and H. Fischer, A., 1910, i, 716; Karrer, A., 1921, i, 310, 313, 768).—The authors question the purity of the acetobromomaltose obtained by Karrer's method, as from this specimen a yield of only 30% of hepta-acetylmaltose is obtainable, whereas from their specimen a 70% yield is produced. Further, the acetobromomaltose obtained by Karrer's method has a very high bromine content, which indicates that some secondary reaction has taken place. Pure acetobromomaltose is prepared by allowing maltose to stand with acetyl bromide for 20—40 minutes at 0°; it is an amorphous solid which after 7 months' drying gave $[\alpha]_D^{15\cdot5}$ +171·5° in chloroform. Hepta-acetylmaltose, microscopic needles, m. p. 174—175°, was obtained by the action of sodium acetate and acetic acid on the bromo compound, the total yield being 70%. The specific rotation increased to a constant value on preservation, and, after 48 hours, is $[\alpha]_D^{10}$ +103·01° in *s*-tetrachloroethane.

Hepta-acetylbenzylmaltoside, colourless prisms, m. p. 125°, $[\alpha]_D^{16\cdot5}$ +27·76° in *s*-tetrachloroethane, was prepared from an absolute ethereal solution of the bromo compound by shaking with silver carbonate and benzyl alcohol. It is hydrolysed by methyl-alcoholic ammonia at 0° to *benzylmaltoside*, m. p. 147—148°, $[\alpha]_D^{17}$ +47·64° in aqueous solution.

Hepta-acetylethylmaltoside, prepared in the same way as the benzyl derivative, crystallises in prisms, m. p. 132°, $[\alpha]_D^{14}$ +48·93° in *s*-tetrachloroethane. It is hydrolysed to *ethylmaltoside*, m. p. 168—169°.

Hepta-acetylmethylmaltoside, m. p. 130—131°, is prepared in the same manner as the ethyl homologue. *Hexa-acetylmaltal* is obtained by the reduction of a solution of the acetobromomaltose in 50% acetic acid by zinc dust at 10°; it crystallises in colourless prisms, m. p. 134°, $[\alpha]_D^{16\cdot5}$ +64·15°. It adds on one atomic proportion of bromine in chloroform solution and on warming with water loses one acetyl group, leaving the penta-acetyl derivative as fine needles, m. p. 123°. This on acetylation with acetic anhydride and pyridine gives a substance, m. p. 113—114°, which has not been further examined.

A. E. C.

Lactosan. A. Pictet and M. M. Egan (*Helv. Chim. Acta*, 1924, 7, 295—297).—When lactose is carefully heated at 120—130° at 4—6 mm., it loses its water of crystallisation, and at 185° in 10 to 12 hours it is converted into the anhydride, *lactosan*, $C_{12}H_{20}O_{10}$, a white, amorphous powder, m. p. 200—202° (decomp.), $[\alpha]_D$ +65·5—66·0°, without mutarotation. It is readily soluble in water, and its reducing power in terms of Fehling's solution is 61% of that of dextrose. Brewer's yeast does not ferment it. With phenylhydrazine, it gives the osazone of lactose, and when acetylated it gives octa-acetyl-lactose. Lactosan is polymerised by heating at 105°/15 mm. for $\frac{1}{4}$ hour with a trace of zinc chloride, forming a *tetralactosan*, $(C_{12}H_{20}O_{10})_4$, m. p. 245—246° (decomp.), which does not reduce Fehling's solution. By fuming hydrochloric acid, lactosan is partly converted into lactosyl chloride. The properties of lactosan indicate that it is ϵ-galactosylglucosan.

E. H. R.

Degradation of Starch by Salts. W. S. Iljin (*Biochem. Z.*, 1924, **145**, 14—17; cf. also Iljin, A., 1923, i, 172; Haehn, A., 1923, i, 443; Biedermann, A., 1923, i, 665).—Further experiments are described in which starch in dilute solution is hydrolysed by various concentrations of sodium, lithium, and calcium chlorides without the intervention of an enzyme. Potassium, magnesium, and barium chlorides are said to give similar results. J. P.

Action of Weak Bases on Cellulose Nitrate. G. G. Giannini (*Gazzetta*, 1924, **54**, 79—85).—Determinations of the compositions and of the molecular weights in freezing acetic acid exhibited by two preparations of the product obtained by Angeli by the action of pyridine on cellulose nitrate (A., 1919, i, 196; 1922, i, 922) containing, respectively, 8·98% and 10·08% N, as well as analyses of the gaseous mixtures emitted during their preparation, suggest that pyridine produces in cellulose nitrate a gradual denitration varying in velocity with the temperature. T. H. P.

Triphenylmethyl Ethers of Cellulose and Starch. B. Helferich and H. Koester (*Ber.*, 1924, **57**, [*B*], 587—591; cf. A., 1923, i, 331).—Cellulose, preferably in the form of material which has been regenerated from the xanthate (1 part), is converted by triphenylmethyl chloride (6 parts) and pyridine (14 parts) at 100° during 14—32 hours into *cellulose triphenylmethyl ether*, $C_{25}H_{24}O_5$, a pale pink, voluminous powder, m. p. about 260° (decomp.), which swells in contact with many organic media and gives colloidal solutions in pyridine, chloroform, and bromoform. Further prolongation of the reaction or use of a larger excess of triphenylmethyl chloride does not lead to the etherification of more hydroxyl groups. The ether is readily hydrolysed by hydrogen chloride in chloroform solution, yielding triphenylmethyl chloride (or the carbinol if water is present) and a carbohydrate which is identical analytically with the original material. If triphenylmethylcellulose is heated with acetic anhydride and pyridine on the water-bath, approximately one acetyl group is introduced into each dextrose component; with chloroacetyl chloride and pyridine, esterification takes place to a greater extent. Rice starch yields *starch triphenylmethyl ether*, $C_{25}H_{24}O_5$, which closely resembles the corresponding cellulose ether. H. W.

Adsorption of Aluminium Hydroxide from Aluminium Sulphate Solutions by Cotton and Wood Cellulose. C. G. Schwalbe (*Z. angew. Chem.*, 1924, **37**, 125—128).—The contradictions which occur in the literature as to whether aluminium hydroxide is adsorbed from aluminium sulphate solutions by cotton and wood cellulose are ascribed to the fact that the adsorptive power of fibres is conditioned by a large number of variable factors such as the period and temperature of steeping, the concentration of the solution in which the fibre is steeped, and especially the previous history of the fibre, circumstances which have an important effect on the nature of its surface. Cotton cellulose which had been stored for 7 years in a dry place failed to adsorb aluminium from solutions of the sulphate or acetate or from sodium aluminate even after milling for 7 hours in a ball mill. In order to study the effects of the presence of hydrocellulose and oxycellulose, strips of cotton fabric were treated with 3% sulphuric acid and heated for 4 hours at 70°, and others were over-bleached before being used in adsorption experiments. The ash content of the samples so treated was found to increase very appreciably after steeping in an aluminium sulphate solution and subsequent washing. It is uncertain whether this increase in the adsorptive power of the fabric is due to the presence of hydrocellulose and oxycellulose or to a change in the nature and extent of the surface. Sized wood cellulose pulp is capable of adsorbing much greater quantities of aluminium hydroxide than the undamaged fibres, and the adsorptive power increases with the fineness of comminution up to a certain point, and thereafter remains approximately constant. The swelling of wood cellulose fibres exerts a great influence on their power of adsorbing aluminium hydroxide. The number of factors which affect the adsorptive power of wood cellulose is even greater than in the case of cotton cellulose, owing to the varying quantities of pentosans and hexosans which may be present. H. C. R.

Quantitative Determination of the Fluorescent Powers (the Spectro-fluorescometry) of Cellulose and its Derivatives. IV. S. J. Lewis (*J. Soc. Dyers and Col.*, 1924, **40**, 111—114).—A continuation of work previously described (this vol., i, 374). No essential differences were found in the fluorescent properties of yarn and ribbon prepared from the same solution of viscose, of hydrocellulose prepared by the action of sulphuric or hydrochloric acid on cotton linters, or of oxycellulose prepared by means of a hypochlorite or potassium permanganate. Experiments with cellulose tendered, by means of acids and exposure to daylight, indicate that changes in fluorescent power appear to be more noticeable in the region of λ 2900. Paper, after exposure for 3 weeks to radium, showed no fluorescence. It is again concluded that the physical condition of the material has but little effect on its fluorescent properties. A. J. H.

Polysaccharides. XXV. Methylation Products of Reserve Cellulose (Lichenin). P. Karrer and K. Nishida (*Helv. Chim. Acta*, 1924, 7, 363—370).—Continuing previous work (this vol., i, 373), fresh evidence is put forward confirming the chemical similarity between lichenin or reserve cellulose and structural cellulose. Exhaustive methylation of lichenin gives a product containing 41·9% of methoxyl, compared with a maximum of 42—43% in the case of cotton. Methylated lichenin dissolves in cold water to a colloidal solution which coagulates on warming. In some respects, it resembles methylated hydrocellulose more than methylated cellulose, but, unlike the former, it does not depress the freezing point of water. The methylated lichenin, when heated with 1% methyl-alcoholic hydrogen chloride, gives trimethyl- and dimethyl-methylglucosides in similar proportions to those obtained from fully methylated cellulose by Irvine and Hirst (T., 1923, **123**, 529). The yield of trimethylglucose obtained by hydrolysis of the glucoside is smaller, however, than the 85% obtained by Irvine and Hirst. E. H. R.

Galegine. E. Späth and S. Prokopp (*Ber.*, 1924, **57**, [*B*], 474—480; cf. Tanret, A., 1914, i, 859).—Galegine is converted by hydrogen in the presence of palladised charcoal to *dihydrogalegine*, $CHMe_2\cdot[CH_2]_2\cdot N{:}C(NH_2)_2$, the constitution of which is deduced from its conversion by barium hydroxide into carbamide and *iso*amylamine and its synthesis from *iso*amylamine and cyanamide. Since galegine on oxidation with permanganate yielded acetone but no trace either of formaldehyde or *iso*butaldehyde, it must have the composition $CMe_2{:}CH\cdot CH_2\cdot N{:}C(NH_2)_2$ (cf. Barger and White, this vol., i, 272). An improved method for the isolation of galegine is described, consisting essentially in extracting the free base from its aqueous solution by means of amyl alcohol. Dihydrogalegine sulphate, white crystals, the *picrate*, yellow crystals, m. p. 173—174°, and m-*nitrobenzoyl* derivative of *iso*amylamine, m. p. 81—82°, are described. F. A. M.

Composition of Japanese Petroleum. I. S. Komatsu and S. Kusumoto (*Mem. Coll. Sci. Kyōto*, 1924, **7**, 77—84).—The fraction of petroleum from Nishiyama, Echigo, distilling below 90°, is shown to consist mainly of methyl*cyclo*pentane, b. p. 71—72°, d_4^{25} 0·7295, n_D^{25} 1·3965, and *cyclo*hexane, b. p. 80—81°, d_4^{25} 0·765, n_D^{25} 1·414. [Cf. *B.*, 1924, 408.] W. A. S.

The Hydrogenating, Reducing, and Oxidising Action of Hydrazine on Organic Compounds. E. Müller and H. Kraemer-Willenberg (*Ber.*, 1924, **57**, [*B*], 575—583).—Benzyl alcohol reacts with 2 mols. of nearly anhydrous hydrazine at 180° to give nitrogen and toluene; if 4 mols. of hydrazine are used, hexahydrotoluene is obtained. At 280° benzene gives *cyclo*hexane, together with a small proportion of adipic acid (the requisite oxygen is derived from the trace of water present in the hydrazine). Toluene, *o*-, *m*-, and *p*-xylenes, mesitylene, and cymene are similarly transformed into their hexahydro-derivatives, hydrogenation occurring under milder experimental conditions with respect to temperature and duration as the number of carbon atoms in the hydrocarbon molecule increases. Pyridine and quinoline are not affected by hydrazine at any temperature up to 330°. Hydrobenzoin yields diphenylethylene oxide, m. p. 56°.

Monohydric phenols are not hydrogenated by hydrazine. At 100°, phenol gives the compound $(Ph\cdot OH)_2,N_2H_4$, m. p. 63°, which is unchanged by hydrazine at 200°. *p*-Cresol and *s*-xylenol yield similar *salts*, the *p*-cresol compound forming colourless needles, m. p. 61—62°. Polyhydric phenols are oxidised by hydrazine, as is evidenced by the copious formation of ammonia. *Quinol hydrazine*, $C_6H_{10}O_2N_2$, long, colourless needles, m. p. 154°, and resorcinol yield solid, nitrogenous products the constitution of which could not be elucidated.

Ethylene glycol is reduced by hydrazine at 200° to ethyl alcohol.

Glycerol is transformed into methyl alcohol, formic, acetic, and racemic acids. Erythritol yields oxalic acid, whereas dulcitol gives a hexose which is converted by phenylhydrazine into an osazone, $C_{18}H_{22}O_4N_4$, pale yellow needles, m. p. 205°. *d*-Mannitol yields dextrose. Cellulose is oxidised by hydrazine. H. W.

The System *cyclo*Hexane–Aniline. E. H. BUCHNER and D. KLEYN (*Rec. trav. chim.*, 1924, **43**, 153—157).—The critical temperatures of mixtures of *cyclo*hexane and aniline containing up to 40·1% of the latter were determined. The curve is regular and on extrapolation gives 427° as the critical temperature of aniline (cf. Guye and Malet, A., 1902, ii, 302). As no maximum was observed, the system is regarded as an exception to the general rule, and doubt is cast on the conclusions drawn by Buchner (A., 1918, ii, 9) in another case. The mutual solubilities of the two substances were also investigated; above 31·3°, there is complete miscibility in all proportions. H. J. E.

Catalytic Preparation of Amines. E. BRINER, P. FERRERO, and E. DE LUSERNA (*Helv. Chim. Acta*, 1924, **7**, 282—294).—Attempts were made to obtain aniline (i) by passing a mixture of benzene and ammonia vapours over a heated catalyst, (ii) from phenol and ammonia in a similar manner. From benzene and ammonia only traces of aniline could be obtained under any conditions; the observations of Wibaut are therefore confirmed (A., 1917, i, 386). The result is only to be expected, as the reaction is endothermic, $C_6H_6+NH_3=NH_2Ph+H_2-23·6$ Cal. The second reaction gives appreciable yields of aniline, up to 12% of the theoretical, the best results being obtained using alumina as catalyst at 420°, with excess of ammonia and prolonged contact. The reaction in this case is exothermic, $PhOH+NH_3=NH_2Ph+H_2O+0·4$ cal. With thoria as the catalyst, only traces of aniline are obtained, but appreciable quantities of diphenyl ether and phenylene oxide; these products are obtained also in absence of ammonia. When methyl alcohol mixed with phenol and ammonia vapours is passed over heated alumina, a mixture of methyl- and dimethyl-anilines is obtained, the former predominating, but the yields are smaller than those from phenol and ammonia alone. In presence of thoria some anisole is formed. E. H. R.

Freezing-point Curves for the System 2-Chloroacetanilide–4-Chloroacetanilide. K. J. P. ORTON and G. OWEN (*J. Chem. Soc.*, 1924, **125**, 766—767).—Owen's method (*J. Chem. Soc.*, 1923, **123**, 3393) has been applied to an examination of the freezing-point curves for the system 2-chloroacetanilide–4-chloroacetanilide. The results were in harmony with the behaviour of the system 2 : 4-dichloroacetanilide–4-chloroacetanilide, the lower-melting polymorph of 4-chloroacetanilide previously observed (*J. Chem. Soc.*, 1909, **95**, 1059) never separating from the liquid mixture in bulk but only when small quantities were cooled very slowly in capillary tubes. R. B.

Action of Hydrogen Chloride on a Dry Solution of a Chloroamine. F. G. SOPER (*J. Chem. Soc.*, 1924, **125**, 768—769).—The action of dry hydrogen chloride on a solution of 2 : 4-dichloro-*N*-chloroacetanilide in glacial acetic acid gives no trace of chlorine except in presence of moisture. This result suggests that hydrolysis, $:NCl+H_2O \rightleftharpoons :NH+HOCl$, is the first step in the production of chlorine and that the appearance of this gas is due to a subsequent interaction, $HCl+HOCl \rightleftharpoons Cl_2+H_2O$. R. B.

Solubility of Anilinesulphonic Acids. J. C. PHILIP and R. S. COLBORNE (*J. Chem. Soc.*, 1924, **125**, 492—500).—The solubility relations previously found to obtain between sulphanilic acid and water (*J. Chem. Soc.*, 1913, **103**, 284) have now been found to be characteristic of the anilinesulphonic acids generally. A notable feature of these acids is the readiness with which they form supersaturated solutions, from which under suitable conditions unstable hydrates may readily be produced. Solubility determinations show that these hydrates are not stable at any temperature on the solubility curve, but are either completely labile or are metastable over a small temperature range in the neighbourhood of 0°. Aniline-*o*-sulphonic acid forms a *monohydrate*, stable below 13·5°; above this temperature, the anhydrous acid is the stable solid phase. Aniline-*m*-sulphonic acid forms a sesquihydrate which separates below 20° as a metastable phase, with a greater solubility than that of the anhydrous acid. *p*-Bromoaniline-*o*-sulphonic acid gives, below 30°, a monohydrate which is metastable with respect to the anhydrous acid even at 0°, although its solubility can be readily measured up to 25°. *p*-Bromoaniline-*m*-sulphonic acid exists in two enantiotropic forms, the rhombic, stable above 100°, the monoclinic, stable at the ordinary temperature, and separation of the metastable monohydrate furnishes the most striking example of the class. This hydrate separates as a felted mass of crystals, which only slowly changes to the less soluble anhydrous acid. *p*-Chloroaniline-*o*-sulphonic acid with water at 0° slowly changes to a stable monohydrate, but no unstable hydrate was observed. *p*-Chloroaniline-*m*-sulphonic acid at 0° forms small tablets of a metastable monohydrate. R. B.

Chemotherapeutical Researches in the Series 205 Baeyer. Carbamates of the Aminobenzoylaminonaphthalenesulphonic Acids. E. FOURNEAU, J. TRÉFOUËL, (MME.) J. TRÉFOUËL, and J. VALLÉE (*Ann. Inst. Pasteur*, 1924, **38**, 81—114).—A more detailed account of work already noted (this vol., i, 382).

Absorption Spectra of some Derivatives of Phenol and other Substances. J. E. PURVIS.—(See this vol., ii, 219.)

Fluorescence Spectra. II. Phenol and Phenolic Ether Vapours. J. K. MARSH.—(See this vol., ii, 219.)

Action of the Oxides and the Oxy-acids of Nitrogen on Diphenyl Ether. H. RYAN and P. T. DRUMM (*Sci. Proc. Roy. Dubl. Soc.*, 1924, **17**, 313—320).—Diphenyl ether treated with nitrogen peroxide alone or in carbon tetrachloride solution, or with nitrous fumes in the same solvent, gave a mixture of *op'*- and *pp'*-dinitrodiphenyl ethers (cf. Mailhe and Murat, A., 1912, i, 346; 1913, i, 44), with some 2 : 4-dinitrophenol; with nitrous fumes in acetic acid solution, the main product was the *p*-mononitro derivative. The latter was also formed when the ether was treated with nitric acid (*d* 1·4) either alone or in carbon tetrachloride or acetic acid. With fuming nitric acid (*d* 1·5) a mixture of the *pp'*-dinitro- and 2 : 2' : 4 : 4'-*tetranitro-diphenyl ether*, m. p. 195°, was formed. This derivative was also obtained from 2 : 4-dinitrochlorobenzene and 2 : 4-dinitrophenol and by further nitration of 2 : 4-dinitrodiphenyl ether and of 2 : 4 : 4'-trinitrodiphenyl ether (cf. Cook, A., 1910, i, 731). 2 : 4 : 6-Trinitrodiphenyl ether (from picryl chloride and potassium phenoxide) and the 2 : 4 : 6 : 2'-tetranitro compound (prepared in a similar way) both gave on further nitration 2 : 4 : 6 : 2' : 4'-*pentanitrodiphenyl ether*, colourless needles, m. p. 210°. W. A. S.

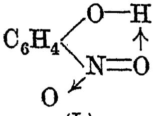
Action of the Oxides and the Oxy-acids of Nitrogen on Phenyl Benzyl Ether. H. RYAN and J. KEANE (*Sci. Proc. Roy. Dubl. Soc.*, 1924, **17**, 287—295).—Treatment of phenyl benzyl ether in the cold, and for a long time if necessary, with nitrogen peroxide, gaseous or in carbon tetrachloride solution, with nitrous fumes or with nitric acid, alone or in carbon tetrachloride solution (cf. A., 1919, i, 13; 1923, i, 323), gave mostly *p*-nitrophenyl benzyl ether, a little *p*-nitrophenyl *p*-nitrobenzyl ether (cf. Kumpf, A., 1884, 1005), and varying amounts of decomposition products. Nitration seemed not to proceed with nitric acid in acetic acid or ether solution. Further nitration of *p*-nitrophenyl benzyl ether was brought about by treatment with nitric acid in carbon tetrachloride solution, but again not in acetic acid or alcohol. The product was the above dinitro derivative. With nitric acid alone, a mixture of o-p-*dinitrophenyl* p-*nitrobenzyl ether*, colourless prisms, m. p. 207—208°, and o-p-*dinitrophenyl* o-*nitrobenzyl ether*, needles, m. p. 188°, was formed. These compounds were also obtained by treating *o*-nitrophenyl benzyl ether in a similar way. Both trinitro derivatives were converted by the action of a mixture of fuming sulphuric and nitric acids into the same product, viz. o-o-p-*trinitrophenyl* o-p-*dinitrobenzyl ether*, scales, m. p. 146°. An attempt to prepare a hexanitro derivative of the ether resulted only in the isolation of a decomposition *product*, m. p. 139—140°. W. A. S.

Action of the Oxides and the Oxy-acids of Nitrogen on Diphenyl Ethylene Ether. H. RYAN and T. KENNY (*Sci. Proc. Roy. Dubl. Soc.*, 1924, **17**, 305—311).—Diphenyl ethylene ether, $Ph{\cdot}O{\cdot}C_2H_4{\cdot}O{\cdot}Ph$, treated with gaseous nitrogen peroxide, or nitrogen peroxide in carbon tetrachloride solution, or with nitric acid (*d* 1·5), alone or in carbon tetrachloride solution, gave mostly the *pp'*-dinitro derivative, m. p. 143° (cf. Weddige, A., 1881, 1136), accompanied by 2 : 4-dinitrophenol and decomposition products. Nitration did not take place with nitric acid dissolved in acetic acid. *Phenyl* o-*nitrophenyl ethylene ether*, rectangular plates, m. p.

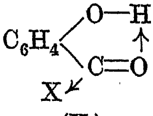
97°, and the corresponding p-*nitro* derivative, prisms, m. p. 86°, were prepared by interaction of the corresponding potassium nitrophenoxide and ω-bromophenetole. Di-*o*-nitrophenyl ethylene ether was prepared similarly (Weddige, *loc. cit.*). From the *o*-nitro and this di-*o*-nitro derivative, by further nitration, o-*nitrophenyl* o-p-*dinitrophenyl ethylene ether*, m. p. 172°, was obtained. All these lower nitrated derivatives gave ultimately *di*-2 : 4-*dinitrophenyl ethylene ether*, pale yellow, flat prisms, m. p. 214°, and continued action of nitric acid destroyed the molecule. o-*Nitrophenyl* p-*nitrophenyl ethylene ether*, rectangular prisms, m. p. 117·5°, was also prepared synthetically. W. A. S.

Solubility of the Aminophenols. N. V. SIDGWICK and R. K. CALLOW (*J. Chem. Soc.*, 1924, **125**, 522—527).—As regards solubility in water and benzene, the aminophenols are an abnormal group, their abnormality resembling that of the phenylenediamines (*Chem. Soc. Trans.*, 1923, **123**, 2817) rather than the usual type. The *o*-compound is less soluble in water than the *p*-isomeride; in benzene, the solubilities are about the same. The *m*-compound is more soluble in water and less soluble in benzene than either of its isomerides. *m*-Aminophenol very readily forms supersaturated solutions in water, consequently it was possible to follow the two-liquid curve up to 60—70° below the saturation point, and even to measure the metastable ice curve in dilute solutions. This appears to be a general property of *m*-derivatives (cf. *Chem. Soc. Trans.*, 1922, **121**, 2256). The following boiling points were determined at 11 mm. pressure: *m*-aminophenol, 164° (with very slight decomp.); *p*-aminophenol, 174° (after melting with decomp.). *o*-Aminophenol sublimes rapidly at 153°. (Cf. following abstract.) R. B.

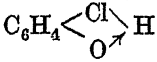
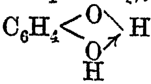
Abnormal Benzene Derivatives. N. V. SIDGWICK and R. K. CALLOW (*J. Chem. Soc.*, 1924, **125**, 527—538).—The results of a series of investigations (*Chem. Soc. Trans.*, 1915, **107**, 1202; 1920, **117**, 389, 396; 1921, **119**, 979, 1001, 1013; 1922, **121**, 1844, 1853, 2256, 2263, 2586; 1923, **123**, 2813, 2819, and preceding abstract) on the volatility and solubility in the liquid state of certain classes of benzene derivatives are summarised and a possible explanation of the phenomena is discussed. The benzene derivatives in question are described as abnormal because the isomerides differ widely in their vapour pressures and solubility relations. Such abnormality depends on the presence in the molecule of two active or alterable substituents (OH, CO_2H, NH_2, CHO, NO_2, Cl, etc., as opposed to unalterable such as the alkyls) and of these two, one must be OH, NH_2 (or substituted NH_2), or CO_2H. Apparently one group makes the compound sensitive and the other augments this sensitiveness. The relations holding among the substituted phenols differ in many respects from those observed with the amines and acids, which again differ from one another. Among the phenols, abnormality was found in all cases examined where the second substituent was other than alkyl. The meta- and para-compounds resemble one another closely as normal isomerides, but differ markedly from the ortho-compounds in being (*a*) less volatile,



(I.)



(II.)

(*b*) more miscible with water, and (*c*) less miscible with benzene, properties characteristic of polar as opposed to non-polar substances. Consideration of other properties confirms the view that the ortho-series is abnormal and from the fact that in these compounds the polar character due to the hydroxylic hydrogen is suppressed in much the same way as if this hydrogen were replaced by methyl, the suggestion is put forward of a co-ordinate linking of the phenolic hydrogen with some atom of the second group. This is expressed in the annexed formulæ, in which the arrow (→) points to the atom receiving the two unshared electrons. These formulæ represent the most stable type of chelate ring known, and formula (II) explains the abnormality of the hydroxybenzoic acids, their esters and aldehydes (X=OH, OAlk, or H). With other active groups (halogens, OH, OAlk, and perhaps NH_2), a five-atom ring must be assumed,  $C_6H_4<\begin{smallmatrix}Cl\searrow\\ O\nearrow\end{smallmatrix}H$ or  $C_6H_4<\begin{smallmatrix}O\searrow\\ O\nearrow\\ H\end{smallmatrix}H$, which is less common, but occurs in the cupferron compounds and is possible in a large class of mordant dyes. Such chelate compounds always tend to be non-polar (cf. acetylacetones) and this ring structure explains why *o*-nitrophenol cannot form compounds with aniline, *p*-toluidine, benzamide, and acetamide, whereas the *m*- and *p*-nitrophenols can; and why if the phenol has an active substituent both in the ortho- and in the para-positions, the influence of the ortho-group predominates and the compound is non-polar. An explanation is also afforded of Auwers' conclusion (A., 1903, ii, 268) that a substituent group which when occupying the ortho-position in a solute gives abnormality, for example, in benzene solution, when introduced into the solvent tends to reduce the abnormality. The behaviour of abnormal derivatives other than phenol is much less easy to explain, and co-ordination through the hydrogen atom is only one of several possibilities. With the chloro- and nitro-acids, the difference between meta- and para-compounds is as great as that between the meta- and ortho-, whilst solubilities both in water and in benzene are in the order $o>m>p$. The amino-compounds are somewhat less abnormal, and this is probably connected with their basicity. The introduction of an acetyl group into the chloro- and nitro-anilines tends to increase the abnormality. Among the amino-compounds the meta-derivative occupies an exceptional position, being less volatile than the para-derivative, and its solubility both in benzene and in water is much nearer to (and sometimes less than) the ortho- than is the case with the other classes of abnormal benzene derivatives, a distinction which points to direct chemical influence rather than to either ring-formation or steric effect. R. B.

Action of the Oxides and Oxy-acids of Nitrogen on β-Naphthyl Ethyl Ether. H. Ryan and J. Keane (*Sci. Proc. Roy. Dubl. Soc.*, 1924, **17**, 297—303).—β-Naphthyl ethyl ether on treatment with nitrogen peroxide, nitrous fumes, or nitric acid in glacial acetic acid or carbon tetrachloride solution, gave mainly 1-nitro-2-naphthyl ethyl ether, and with gaseous nitrogen peroxide or nitric acid (more than before) in carbon tetrachloride solution or alone, a mixture of 1 : 6- and 1 : 8-dinitro-2-naphthyl ethyl ether. The ether itself, its 1-nitro-, 1 : 6-dinitro-, and 1 : 8-dinitro-derivatives were all converted by the further action of nitric acid into 1 : 6 : 8-*trinitro-2-naphthyl ethyl ether*, colourless prisms or scales, m. p. 189—190° (cf. Staedel, A., 1883, 863), the constitution of which was thus proved. Heated with alcoholic ammonia, it gave 1 : 6 : 8-trinitro-β-naphthylamine, m. p. 300—301°. W. A. S.

Conversion of Eugenol into *iso*Eugenol. S. K. Gokhale, J. J. Sudborough, and H. E. Watson (*J. Indian Inst. Sci.*, 1923, 6, 241—255).—The composition of mixtures of eugenol and *iso*-eugenol is best estimated from the refractive index. The earlier method (McKie, *Chem. Soc. Trans.*, 1921, **119**, 777) is troublesome and untrustworthy. Eugenol has n_D^{30} 1·53664 and *iso*eugenol n_D^{30} 1·57237. The curve showing the relationship between composition and refractive index for mixtures is a straight line. The temperature coefficient of the refractive index is about 0·0004 per degree for both substances.

When eugenol is fused with sodium hydroxide at 200—210°, little if any conversion and much decomposition takes place; with potassium hydroxide (4 parts), 85% of the theoretical yield of *iso*eugenol is obtained (cf. Einhorn and Frey, A., 1894, i, 578). A mixture of 2 parts of sodium hydroxide and 1 part of potassium hydroxide also gives a good yield. When eugenol is heated with 6 to 8 parts of 50% potassium hydroxide solution in an autoclave at 170—180°, almost complete conversion takes place. W. A. S.

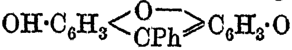
Adrenaline Compounds. C. Funk and L. Freedman (U. S. Pat. 1472298).—β-*Methylamino*-4-α-*ethoxyethylpyrocatechol hydrochloride*, thin, rectangular prisms, m. p. 169°, is prepared by heating *r*-adrenaline (or its hydrochloride) for several hours in a reflux apparatus with absolute ethyl alcohol containing dry hydrogen chloride equivalent to 1—4 mols. of adrenaline, and cooling. A *substance* (*hydrochloride*, rectangular prisms, m. p. 180—183°), possibly a lactonic compound of 2 mols. of adrenaline, is also formed.

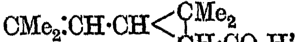
Chemical Abstracts.

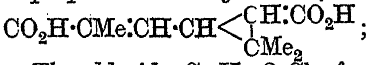
Properties of Neighbouring Hydroxy Groups Attached to a Benzene Nucleus. R. L. Alimchandani (*J. Chem. Soc.*, 1924, **125**, 539—543).—The hypothesis that the carbon atoms of the benzene nucleus are charged alternately positively and negatively finds support in the properties of the three vicinal methoxy groups of 3 : 4 : 5-trimethoxy-2-trichloromethylphthalide and 3 : 4 : 5-trimethoxybenzenesulphonic acid. When chloral hydrate is condensed with 3 : 4 : 5-trimethoxybenzoic acid by means of 90% sulphuric acid, the product consists mainly of 3 : 4 : 5-trimethoxy-2-trichloromethylphthalide, rectangular plates, m. p. 76—77°, from which the simultaneously formed 4-hydroxy-3 : 5-dimethoxy-2-trichloromethylphthalide is separated by means of dilute sodium hydroxide. The trimethoxyphthalide by treatment with 98% sulphuric acid is converted into 4-hydroxy-3 : 5-dimethoxy-2-trichloromethylphthalide, m. p. 172—173°, and with sodium hydroxide into 3 : 4 : 5-trimethoxyphthalide-2-carboxylic acid, m. p. 147—149°. Hydrolysis of this acid with 96—98% sulphuric acid gives 4-hydroxy-3 : 5-dimethoxyphthalide-2-carboxylic acid. 3 : 4 : 5-Trimethoxyphthalide similarly yields 4-hydroxy-3 : 5-dimethoxyphthalide, m. p. 144°. The action of 96—98% sulphuric acid on pyrogallyl trimethyl ether gives in varying proportions 3 : 4 : 5-*trimethoxybenzenesulphonic acid*, leaflets, containing $1{\cdot}5H_2O$, m. p. 95—97° (the *barium*, *sodium*, and potassium salts are described), and 4-*hydroxy*-3 : 5-*dimethoxybenzenesulphonic acid*, leaflets, $1{\cdot}5H_2O$, m. p. 128—129° (the *barium* and sodium salts are described), which is not hydrolysed by sulphuric acid even in hot solution and on oxidation yields 2 : 6-dimethoxy-*p*-benzoquinone. Treatment with bromine gives 1 : 2 : 3-*tribromo*-5-*hydroxy*-4 : 6-*dimethoxybenzene*, slender prisms, m. p. 134—135°, which by methylation with methyl sulphate gives 1 : 2 : 3-tribromo-4 : 5 : 6-trimethoxybenzene, prisms, m. p. 75—76°. This compound was also obtained by the action of bromine on 3 : 4 : 5-trimethoxybenzenesulphonic acid, the sulphonic group being displaced. Hydrolysis of the trimethoxybenzenesulphonic acid to pyrogallyl trimethyl ether readily takes place in hot sulphuric acid. R. B.

Methyl Ether of Diphenylphenylacetylenylcarbinol. K. Ziegler and K. Tripp (*Ber.*, 1924, **57**, [*B*], 420; cf. A., 1923, i, 921).—The carbinol is readily methylated by dissolving it in hot methyl alcohol and adding 1 to 2% of sulphuric acid, previously diluted with methyl alcohol. On cooling, the methyl ether crystallises out almost quantitatively, and after recrystallisation forms leaflets, m. p. 123—124°. It is decomposed by acids to give phenyl β-phenylstyryl ketone, m. p. 86—87° (cf. A., 1922, i, 556). F. A. M.

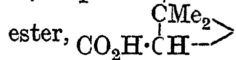
Benzeins. R. Meyer and W. Gerloff (*Ber.*, 1924, **57**, [*B*], 591—599; cf. A., 1923, i, 230).—Benzaurin dissolves in aqueous alkali to an intense carmine solution which gradually fades; the fading is not due to atmospheric action as suggested by Doebner (*Ber.*, 1879, **12**, 1464), but probably to the transformation of coloured *p*-hydroxyfuchsone into colourless dihydroxytriphenylcarbinol. On passing carbon dioxide into the colourless solution, the original benzaurin is reprecipitated. It is considered to be *p*-hydroxyfuchsone hydrate, $OH{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}O,H_2O$. Benzaurin forms a crystalline *bisulphite* compound, $(OH{\cdot}C_6H_4)_2C(Ph)SO_3Na$, which decomposes on keeping. It was not found possible to prepare an oxime, phenylhydrazone, or semicarbazone. Treatment of an alkaline solution of benzaurin with potassium cyanide gave the *nitrile*, $(OH{\cdot}C_6H_4)_2C(Ph)CN$, an oil which slowly solidified to crystals, m. p. 203—204°; attempts to hydrolyse the nitrile to the corresponding dihydroxytriphenylmethanecarboxylic acid were unsuccessful. On treatment with acetic anhydride, the nitrile yielded a *diacetyl* derivative, colourless crystals, m. p. 140—141°, and on benzoylation gave *dihydroxytriphenylmethanecarboxylamide dibenzoate*, $(OBz{\cdot}C_6H_4)_2C(Ph)CONH_2$; on hydrolysing this with alcoholic potassium hydroxide and acidifying the resultant solution, the original nitrile was recovered. *Benzaurin diethyl ether* and *dibenzyl ether* are colourless, crystalline substances melting at 75—76° and 110°, respectively. Bromination of benzaurin in acetic acid in presence of iron gives *tetrabromobenzaurin*, dark red crystals which lose no water on moderate heating (*sodium* salt, brown needles with green iridescence). Benzaurin is reduced by alcoholic ammonia to *pp'*-diaminotriphenylmethane; using strong aqueous ammonia, *p*-aminofuchsonimine is formed.

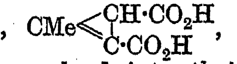
Resorcinolbenzein dried in a vacuum has the formula $C_{19}H_{14}O_4$. At 140°, it loses 1 mol. of water, leaving a product, $C_{19}H_{12}O_3$, as found by Kehrmann; the authors therefore give the hydrated substance the formula  $OH{\cdot}C_6H_3{<}\overset{O\text{—}}{\underset{CPh}{}}{>}C_6H_3{\cdot}O\ .\ .\ .\ H_2O$. The following derivatives of resorcinolbenzein were prepared: *diacetate*, yellow needles, m. p. 145°; *dibenzoate*, colourless needles, m. p. 152°; dibromo derivative, reddish-yellow powder which loses H_2O at 140°; tetrabromo derivative, crystals which lose 1 mol. of HBr at 140—150°; *pentabromo* derivative, brown needles, which sublime with decomposition at 140—150° (*sodium salt*, brownish-red needles with green iridescence). *Dinitroresorcinolbenzein nitrate*, obtained by warming the benzein with strong nitric acid, forms a brilliant red, crystalline powder which decomposes with a slight explosion on heating. F. A. M.

Insecticides. II. Constitution of Chrysanthemum-mono- and -di-carboxylic Acids. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 201—211).—Three acids were obtained by hydrolysis of the semicarbazones of the active constituents of insect powder (cf. p. 523). The first, chrysanthemumcarboxylic acid, $C_{10}H_{16}O_2$, is readily separated from the others on account of its volatility in steam, and is shown to be 2 : 2-*dimethyl*-3-iso*butenyl*cyclo*propane*-1-*carboxylic acid*,  $CMe_2{:}CH{\cdot}CH{<}\begin{matrix}CMe_2\\ |\\ CH{\cdot}CO_2H\end{matrix}$, $[\alpha]_D^{20}$ +20·1°. Its *methyl* ester is a colourless liquid, b. p. 99°/14 mm., 86—87°/10 mm., $[\alpha]_D^{20}$ +20·74°, having a faint odour of insect powder; *chloride*, $C_{10}H_{15}OCl$, colourless oil, b. p. 85°/12 mm., 58°/0·03 mm.; *anilide*, white needles, m. p. 101°; *amide*, white needles, m. p. 131°; *anhydride*, viscous oil, b. p. 125°/15 mm. When reduced by the Paal-Skita method, the acid takes up two atoms of hydrogen, giving 2 : 2-*dimethyl*-3-iso*butyl*cyclo*propane*-1-*carboxylic acid*, a colourless, mobile oil, b. p. 124—126°/10 mm. Its *chloride* has b. p. 89—90°/12 mm.; *amide*, white crystals, m. p. 132—132·5°; and *anilide*, large, colourless crystals, m. p. 82—83°. *Methyl* 1-trans-*caronate*, $C_9H_{14}O_4$, obtained by decomposing chrysanthemumcarboxylic acid ozonide, forms a mass of white crystals, m. p. 37—38°, b. p. 93°/25 mm., $[\alpha]_D$ −8·26° in benzene. The second acid obtained from insect powder, chrysanthemumdicarboxylic acid, has the composition $C_{10}H_{14}O_4$, and the third, $C_{11}H_{16}O_4$, is its monomethyl ester. It is the latter which is present in the active constituent of the insect powder, the former being formed from it by hydrolysis. By the action of ozone, the second acid gives *l-trans*-caronic acid and pyruvic acid, whilst the third gives *l-trans*-caronic acid and methyl pyruvate. Chrysanthemumdicarboxylic acid is therefore 2 : 2-*dimethyl*-3-β-*carboxypropenyl*cyclo*propane*-1-*carboxylic acid*,



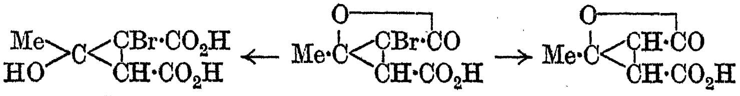
$$CO_2H\cdot CMe{:}CH\cdot CH{<}\begin{matrix}CH\cdot CO_2H\\ |\\ CMe_2\end{matrix};$$

it has $[\alpha]_D^{17}$ +72·8°. The *chloride*, $C_{10}H_{12}O_2Cl_2$, forms white crystals, m. p. 48—50°, b. p. 151°/12 mm.; *anilide*, m. p. 204—205°. The *monomethyl* ester,  $\begin{matrix}CMe_2\\ |\\ CO_2H\cdot CH\end{matrix}{>}CH\cdot CH{:}CMe\cdot CO_2Me$, is a viscous oil, b. p. 129—130°/0·03 mm., $[\alpha]_D^{18}$ +103·9°; the *chloride* is a colouroil, b. p. 114°/0·5 mm. The *dimethyl* ester is a colourless oil, b. p. 149°/16 mm., 87—88°/0·25 mm. When chrysanthemumdicarboxylic acid is distilled at atmospheric pressure, it partly decomposes into carbon dioxide and 2 : 2-*dimethyl*-3-*propenyl*cyclo*propane*-1-*carboxylic acid*, a mobile oil, b. p. 133°/12 mm.; *chloride*, b. p. 95°/12 mm. With pyrethrolone, this acid forms an ester having weak insecticidal properties. The ester obtained from reduced chrysanthemumcarboxylic acid and pyrethrolone is inactive. E. H. R.

3-Methyl*cyclo*propene-1 : 2-dicarboxylic Acid. F. FEIST (*Annalen*, 1924, **436**, 125—153; cf. Feist, A., 1893, i, 404; Goss, Ingold, and Thorpe, *J. Chem. Soc.*, 1923, **123**, 327).—When bromo*iso*dehydracetic acid is treated with alkali, an acid (A) is produced, m. p. 200°, which on dibromination and reduction with sodium amalgam yields an isomeride (B), m. p. 189°. Only one formula is possible for both these isomeric methyl*cyclo*propenedicarboxylic acids, namely,  $CMe{<}\begin{matrix}CH\cdot CO_2H\\ |\\ C\cdot CO_2H\end{matrix}$, since both are racemic acids which can be resolved into their optically active components. The acid A (*silver* salt, and *phenylhydrazine* salt, white needles, m. p. 138°) was resolved by means of its quinine salt into *d*- and *l*-acids having the rotations $[\alpha]_D$ +215° and −156°. They both melt at 200°. The methyl ester, needles, m. p. 32°, has b. p. 122°/20 mm., d_4^{20} 1·142, n_D^{20} 1·4672. The ethyl ester, m. p. 38°, b. p. 135°/15 mm., the *anilide*, white powder, m. p. 246°, and *carbamide* salt, m. p. 215°, are described.

The acid B was resolved by means of its brucine and quinine salts; the extreme values obtained for the *d*- and *l*-acids were $[\alpha]_D$ +179·8° and −118°. The methyl ester of B has m. p. 30·5° and b. p. 116°/20 mm.; d_4^{20} 1·140, n_D^{20} 1·4669. It is not identical with the methyl ester of A and on hydrolysis regenerates B. The latter is converted into A by concentrated sulphuric acid or by heating with concentrated alkali.

By dibromination of the acids or their esters and subsequent reduction with sodium amalgam, B is produced. The dibromo-acid derived from A melts at 244° and gives an *ethyl* ester, b. p. 183—184°/13 mm., d_4^{20} 1·590, n_D^{20} 1·5026. The *methyl* ester forms white needles, m. p. 77°. The dibromo-acid derived from B melts at 232° and yields an *ethyl* ester, b. p. 177°/13 mm., d_4^{20} 1·566, n_D^{20} 1·500. This dibromo-acid on warming with water or concentrated alkali yields a monobasic lactonic acid, $C_6H_5O_4Br$, m. p. 171°, *2-bromo-3-hydroxy-3-methyl*cyclo*propane-*1 : *3-dicarboxylolactonic acid* (I), which is readily transformed by alkali into the corresponding hydroxy-acid, $C_6H_7O_5Br$ (II). The *methyl* ester of the lactonic acid has m. p. 98°, b. p. 166°/15 mm. By reduction of the lactonic acid with sodium amalgam, bromine is removed and the lactone of so-called oxalbutyric acid, m. p. 140—141°, is left (III).



(II.) (I.) (III.)

The lactonic acid (m. p. 171°) is identical with the lactone of so-called oxalbromobutyric acid. On oxidation with alkaline permanganate, it yields a tribasic *acid*, $C_6H_5O_6Br$ (m. p. 225°), which gives a *dimethyl* ester, m. p. 76°.

Reduction of 3-methyl*cyclo*propene-1 : 2-dicarboxylic acids (A or B) by means of colloidal palladium and hydrogen yields two isomeric 3-methyl*cyclo*propane-1 : 2-dicarboxylic acids (m. p. 147° and 108°). A third isomeride, m. p. 138—140°, has also been obtained as a by-product in the reduction of the dibromomethyl*cyclo*propanedicarboxylic acid by means of sodium amalgam. Of the three possible isomerides, two have been already described, one, m. p. 108°, by Preiswerk (A., 1903, i, 459), and the other by Kötz and Stalmann (A., 1903, i, 741), who isolated a syrup. The acid, m. p. 147°, is thought to be the *trans* acid, as it gives no anhydride. The methyl ester has b. p. 208·5—209°/760 mm., 100°/14 mm., and on hydrolysis yields an acid, m. p. 138°. The acid, m. p. 147°, after exposure to moisture melts at 138°, but after drying its melting point rises to 147°. Acid A gives an *ozonide*, $C_6H_6O_7$ (horny solid), which on hydrolysis yields oxalic and acetic acids, through acetyloxalacetic acid. The methyl ester gives an *ozonide* (colourless oil) which on hydrolysis yields methyl acetoacetate and methyl oxalacetate.

A. E. C.

Anhydrides. W. AUTENRIETH and G. THOMAE. (See i, 485).

Constitution of Sparassol. A. ST. PFAU (*Ber.*, 1924, 57, [*B*], 468—470).—The product, m. p. 67—68° (sparassol), obtained by Wedekind and Fleischer (this vol., i, 174) from the fungus *Sparassis ramosa*, is proved to be identical with a product obtained by Pfau from a fungus, *Evernia prunastri*. It is identical with the methyl ester of everninic acid, 6-hydroxy-4-methoxy-*o*-toluic acid, and is not methyl 4-hydroxy-6-methoxy-*o*-toluate as suggested by Wedekind and Fleischer. Sparassol does not exist as such in the fungus, but is formed by the alcoholysis of the evernic acid present. On hydrolysis with 10% aqueous sodium hydroxide, sparassol yields everninic acid. F. A. M.

Sparassol. E. Späth and K. Jeschki (*Ber.*, 1924, **57**, [*B*], 471–474; cf. preceding abstract).—The constitution of sparassol was proved in the following manner. Orcinol was converted into orcylaldehyde by the method of Gattermann and Köbner (A., 1899, i, 363) and this into orsellinic acid (4 : 6-dihydroxy-*o*-toluic acid). The last was methylated by means of diazomethane to the 4-methyl ether of methyl orsellinate (methyl everninate), which melted at 67—68° and was identical with Wedekind and Fleischer's sparassol. The *acetyl* derivative (*acetylsparassol*) has m. p. 63—64°. The *dimethyl* ether of methyl orsellinate has m. p. 41—42°, and the *nitro* derivative of methyl everninate, m. p. 168—169°. F. A. M.

Physical Constants of Stereoisomeric Compounds. K. von Auwers and B. Ottens (*Ber.*, 1924, **57**, [*B*], 437—446).—Systematic investigation of the benzenoid hydrocarbons (cf. A., 1916, i, 130; 1919, i, 578) and of derivatives of *cyclo*hexane (A., 1920, i, 721) has shown that the propinquity of side chains or other substituents to one another causes an increase in density and index of refraction and a decrease in molecular refractivity. It is to be expected, therefore, that the *cis*-forms of stereoisomeric compounds as a consequence of the closer juxtaposition of their substituents would resemble the ortho- or 1 : 2-derivatives and have a higher density and refractive index but a lower molecular refraction than their *trans*-isomerides. This hypothesis has already been utilised to some extent in the elucidation of the configuration of compounds (cf. Skita, A., 1920, i, 27; 1923, i, 671; Hückel, this vol., i, 31); its general validity is now tested by an examination of several well-defined pairs of isomerides.

Ethyl hexahydrophthalate and ethyl 4-amino-2 : 6 : 6-trimethylhexahydrobenzoate exhibit well-marked differences which are in harmony with the rule mentioned above; with the ethyl esters of hexahydroterephthalic and hexahydrohomophthalic acids, the differences are so slight as to be inconclusive, whilst with the ethyl hexahydro*iso*phthalates the slight differences are contrary to the rule. The latter observation, combined with the experience of Skita (A., 1923, i, 671), indicates that for the present physical data cannot be regarded as trustworthy aids in elucidating the configuration of meta- or 1 : 3-derivatives. The values observed with trithioaldehyde and trithioacetone are in harmony with those which are anticipated; this is also the case with the isomeric βε-dihydroxy-βε-dimethyl-Δγ-hexenes, $OH\cdot CMe_2\cdot CH{:}CH\cdot CMe_2\cdot OH$ (cf. Zalkind, A., 1923, i, 176). The stereoisomeric dimethylsuccinic and dimethylglutaric esters show similar small, scarcely utilisable differences in their constants such as are observed with the hydrogenated tere- and homo-phthalic esters. The further accumulation of methyl groups in the succinic molecule produces the expected effects. The physical constants of pairs of stereoisomeric alkyl-glutaconic esters are very similar. This is to be expected if Feist's view that these substances are geometrical isomerides is accepted, since marked differences in the spectroscopic constants are only observed with simple, stereoisomeric acids and esters of the acrylic series, and these tend to disappear as the molecule becomes more complicated, even to only a limited extent. On the other hand, exaltations such as would be expected if Thorpe's formulation is adopted are not observed.

Physical constants are recorded for the following compounds. *Ethyl* cis-*hexahydrophthalate*, b. p. 133°/10 mm., d_4^{20} 1·054, $n_\alpha^{13{\cdot}9}$ 1·45296, n_{He}^{20} 1·453. *Ethyl* trans-*hexahydrophthalate*, b. p. 135°/11 mm., d_4^{20} 1·040, n_{He}^{20} 1·450. *Ethyl* cis-*hexahydro*iso*phthalate*, b. p. 142°/11 mm., d_4^{20} 1·045, n_{He}^{20} 1·452. *Ethyl* trans-*hexahydro*iso*phthalate*, b. p. 142°/12 mm., d_4^{20} 1·047, n_{He}^{20} 1·453. *Ethyl* cis-*hexahydroterephthalate*, b. p. 151°/13 mm., $d_4^{20{\cdot}6}$ 1·0516, $n_{\mathrm{He}}^{20{\cdot}6}$ 1·45222. *Ethyl* trans-*hexahydroterephthalate*, lustrous, flattened needles, m. p. 43—44°, $d_4^{64{\cdot}4}$ 1·0105, $n_{\mathrm{He}}^{64{\cdot}4}$ 1·43367. *Ethyl* cis-*hexahydrohomophthalate*, b. p. 273°, d_4^{20} 1·040, n_{He}^{20} 1·454. *Ethyl* trans-*hexahydrohomophthalate*, b. p. 275°, d_4^{20} 1·038, n_{He}^{20} 1·453. Ethyl *cis*-4-amino-2 : 6 : 6-trimethylhexahydrobenzoate, b. p. 127°/11 mm., d_4^{20} 0·990, n_{He}^{20} 1·475. Ethyl *trans*-4-amino-2 : 6 : 6-trimethylhexahydrobenzoate, b. p. 127°/11 mm., d_4^{20} 0·980, n_{He}^{20} 1·473.

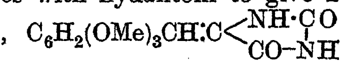
Ethyl succinate, b. p. 217°, d_4^{20} 1·041, n_{He}^{20} 1·420. Ethyl methylsuccinate, b. p. 218°, d_4^{20} 1·011, n_{He}^{20} 1·419. Ethyl *cis*-αβ-dimethylsuccinate, b. p. 221°, d_4^{20} 0·996, n_{He}^{20} 1·423. Ethyl *trans*-αβ-dimethylsuccinate, b. p. 220°, d_4^{20} 0·995, n_{He}^{20} 1·421. Ethyl αα-dimethylsuccinate, b. p. 218°, d_4^{20} 0·993, n_{He}^{20} 1·421. *Ethyl trimethylsuccinate*, b. p. 226°, d_4^{20} 0·993, n_{He}^{20} 1·436. Ethyl tetramethylsuccinate, b. p. 219°, d_4^{20} 0·995, n_{He}^{20} 1·436. *Ethyl* cis-αγ-*dimethylglutarate*, b. p. 231°, d_4^{20} 0·980, n_{He}^{20} 1·423. *Ethyl* trans-αγ-*dimethylglutarate*, b. p. 231°, d_4^{20} 0·977, n_{He}^{20} 1·422.

Ethyl *cis*-β-methylglutaconate, b. p. 131°/19 mm., d_4^{20} 1·034, n_{He}^{20} 1·452. Ethyl *trans*-β-methylglutaconate, b. p. 127°/12 mm., d_4^{20} 1·034, n_{He}^{20} 1·452. Ethyl *cis*-αβ-dimethylglutaconate, b. p. 128°/13 mm., d_4^{20} 1·024, n_{He}^{20} 1·454. Ethyl *trans*-αβ-dimethylglutaconate, b. p. 125°/12 mm., d_4^{20} 1·031, n_{He}^{20} 1·454. Ethyl *cis*-α-ethyl-β-methylglutaconate, b. p. 127°/12 mm., d_4^{20} 1·019, n_{He}^{20} 1·455. Ethyl *trans*-α-ethyl-β-methylglutaconate, b. p. 139°/18 mm., d_4^{20} 1·014, n_{He}^{20} 1·453.

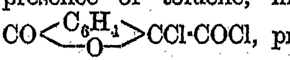
Trithioacetone, $C_9H_{18}S_3$, has m. p. 22°, d_4^{20} 1·068, n_{He}^{20} 1·542. *cis*-Trithioacetaldehyde, m. p. 101°, and *trans*-trithioacetaldehyde, m. p. 126°, in addition to trithioacetone have been examined in quinoline solution; the solvent is shown to be suitable for this purpose.

cis-βε-Dihydroxy-βε-dimethylhexene, m. p. 76°, d_4^{99} 0·869, n_{He}^{99} 1·423. *trans*-βε-Dihydroxy-βε-dimethylhexene, m. p. 69°, d_4^{99} 0·864, n_{He}^{99} 1·422.

H. W.

Synthesis of Polyhydroxyphenylalanines. F. SCHAAF and A. LABOUCHÈRE (*Helv. Chim. Acta*, 1924, 7, 357—363).—For the synthesis of 2 : 5-dihydroxyphenylalanine, gentisaldehyde dimethyl ether (2 : 5-dimethoxybenzaldehyde) was condensed with hippuric acid, and the resulting α-benzoylamino-2 : 5-dimethoxycinnamic acid reduced to α-benzoylamino-2 : 5-dimethoxy-β-phenylpropionic acid, from which the 2 : 5-dihydroxyphenylalanine was obtained. This method was inapplicable for the synthesis of trihydroxyphenylalanine as the cinnamic acid derivative could not be reduced. The following method was, however, successful. 2 : 3 : 4-*Trimethoxybenzaldehyde* was obtained by Gattermann's synthesis from pyrogallol and hydrocyanic acid; it forms glistening prisms, m. p. 37°. It condenses with hydantoin to give 2 : 3 : 4-*trimethoxybenzylidenehydantoin*,  $C_6H_2(OMe)_3CH{:}C<\begin{matrix}NH\cdot CO\\ CO-NH\end{matrix}$, pale yellow needles, m. p. 197°, which is reduced by sodium amalgam in water to 2 : 3 : 4-*trimethoxybenzylhydantoin*, thin, white needles, m. p. 154°. This is hydrolysed by boiling barium hydroxide to 2 : 3 : 4-*trimethoxyphenylalanine*, forming star-shaped aggregates of needles, m. p. 216°. If the hydrolysis is not carried to completion, *α-carbamido-*β-2 : 3 : 4-*trimethoxyphenylpropionic acid* is obtained, m. p. 189°. The trimethoxyphenylalanine is demethylated by boiling with hydriodic acid (*d* 1·70), giving 2 : 3 : 4-*trihydroxyphenylalanine*, crystallising in short, stout needles, m. p. 225° (decomp.). Its neutral solution reduces silver nitrate in the cold and gives a permanent blue colour with ferric chloride.

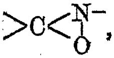
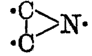
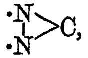
3 : 4 : 5-*Trihydroxyphenylalanine* was synthesised in a similar manner. It forms stout prisms, m. p. 290° (decomp.). In its low solubility it resembles 3 : 4-dihydroxyphenylalanine, but both the trihydroxyphenylalanines differ from this in not giving the characteristic reaction with the pigment-forming ferment, dopaoxydase. 3 : 4 : 5-*Trimethoxybenzylidenehydantoin* forms yellow needles, decomp. 250—260°; 3 : 4 : 5-*trimethoxybenzylhydantoin*, long, white prisms, m. p. 172°; 3 : 4 : 5-*trimethoxyphenylalanine*, white needles, decomp. 220°. E. H. R.

Constitution of Phthalonic Acid. CORNILLOT (*Compt. rend.*, 1924, **178**, 713—715; cf. this vol., i, 294).—Phthalonic anhydride (1 mol.) is converted by phosphorus pentachloride (1 mol.), in presence of toluene, into *α-chlorophthalide-α-carboxylic chloride*,  $CO<\begin{matrix}C_6H_4\\ O\end{matrix}>CCl\cdot COCl$, prisms, m. p. 70°, b. p. 120°/2 mm. The latter in moist air passes into the corresponding *acid*, white needles, m. p. 133°. The acid is stable in air; cold alkali slowly, and warm alkali very rapidly, affords phthalonic acid. The chloro-acid, or its chloride, is at once converted by alcohols into the corresponding esters. The *methyl* ester, stable, has m. p. 92°; the *ethyl* ester, m. p. 48°, b. p. 164°/5 mm., is gradually affected by moist air. The chloride, with aniline, affords the corresponding *anilide* (m. p. 137·5°), this being converted by concentrated alkali into phthalonanilic acid.

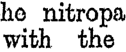
Phthalonic anhydride and methyl alcohol afford *methyl hydrogen phthalonate*, $C_6H_4(CO_2H)\cdot CO\cdot CO_2Me$, m. p. 94°; this ester separates from alcoholic solutions with 1 mol. of solvent of crystallisation (removable in a vacuum), and is converted by phosphorus pentachloride into methyl α-chlorophthalide-α-carboxylate. E. E. T.

Isomerism of the Oximes. XVI. Action of Ultra-violet Light on Aldoximes and their Derivatives. O. L. Brady and G. P. McHugh (*J. Chem. Soc.*, 1924, **125**, 547—554).—The action of ultra-violet light on nineteen aromatic aldoximes has been investigated. In nine cases, viz., *p*-methoxy- and 3 : 4-methylenedioxybenz*anti*aldoximes, benz*anti*aldoxime, *o*-, *m*-, and *p*-nitro-, and *o*-, *m*-, and *p*-chloro-benz*anti*aldoximes, conversion from the *anti*- to the *syn*-isomeride was accomplished, but in all these cases the *syn*-isomeride has been prepared by other means. It is evident, however, that the conversion is not dependent, as Ciusa supposed (A., 1907, i, 137), on the presence of a negative substituent in the benzene ring. Eight cases were examined in which the *syn*-isomeride had not been prepared by other means: *o*-methoxy-, 5-bromo-*o*-methoxy-, 2 : 4-dinitro-, 3-nitro-*p*-dimethylamino-, 6-nitro-3 : 4-methylenedioxy-, 5-nitro-3 : 4-dimethoxy-, 6-nitro-3 : 4-dimethoxy-, and 5-bromo-4-hydroxy-3-methoxy-benz*anti*aldoximes, and in no case did conversion take place under the influence of ultra-violet light. With 3 : 4-dimethoxybenz*anti*aldoxime no isomeric change occurred, although the *syn*-compound has been obtained by special means. 5-Bromo-3 : 4-dimethoxybenz*anti*aldoxime suffered demethylation when exposed to ultra-violet light, giving 5-bromo-4-hydroxy-3-methoxybenz*anti*aldoxime.

A number of derivatives of the *anti*-oximes have been examined, and of these the three *O*-ethers, viz., the methyl ethers of *m*- and *p*-nitrobenz*anti*aldoximes and the benzyl ether of *p*-nitrobenz*anti*aldoxime, were converted into the *syn*-isomeride, although not so completely as the oximes. Of the two nitrogen ethers investigated, the *N*-methyl ether of benzaldoxime is decomposed, yielding benzonitrile, whilst the *N*-methyl ether of *m*-nitrobenzaldoxime undergoes no change. R. B.

Configuration of Stereoisomeric Oximes and the Structure of Oxime-*N*-ethers and *aci*-Nitro Derivatives. K. von Auwers and B. Ottens (*Ber.*, 1924, **57**, [*B*], 446—461).—The spectrochemical behaviour of a series of oximes is found to be closely similar to that of their *O*-alkyl and acyl derivatives. Since the latter substances necessarily contain the group $\colon C\colon N\cdot OR$, it follows that the oximes themselves must have the constitution $\colon C\colon N\cdot OH$. Confirmation of this view is found in the observation that the benzylideneamines, which undoubtedly contain the similar, conjugated group, $\cdot C\colon C\cdot CH\colon N-$, have molecular exaltations which are of the same order of magnitude as those of the oximes. A consideration of the magnitudes of the physical constants of the oximes renders it very improbable that a three-membered ring,  $>C<\overset{N-}{\underset{O}{|}}$, is present, although a direct estimation of the influence of the ring is impossible, since there is no known compound in which its presence has been established definitely. It is, however, scarcely conceivable that such a ring, even when conjugated with a double linking, could produce the observed remarkable increase in index of refraction and dispersive power, particularly since heterocyclic rings containing nitrogen, such as  $\begin{matrix}\cdot C\\ |\\ \cdot C\end{matrix}\!>\!N\cdot$ and  $\begin{matrix}\cdot N\\ |\\ \cdot N\end{matrix}\!>\!C$, are optically indifferent. The "nitrone" formula, $:C:NH:O$, for the oximes is excluded, since their *N*-ethers are characterised by unusually high dispersive power, which could scarcely fall to a small fraction in the oximes themselves if the latter substances yielded the *N*-ethers simply by the replacement of hydrogen by alkyl without any structural change.

Attempts to discriminate between the *cis*- and *trans*-forms of stereoisomeric oximes, on the hypothesis that the former varieties exhibit higher densities and refractive indices but smaller molecular refractions and dispersions than the *trans*-compounds, are described. In the cases of the benzaldoximes and their ethers, it is found that the α-oxime has the *syn*-configuration; this is opposed to the customary view, but is in harmony with the recent observations of Meisenheimer (A., 1922, i, 152) and Beckmann (A., 1923, i, 228). In a number of other instances, the interpretation of the observed results is much more difficult; at present, it is not possible to form a definite opinion as to the value of spectrochemical evidence in this field.

The optical behaviour of the *N*-ethers of oximes is strongly against the existence of a three-membered ring,  $:C<\begin{matrix}N\cdot R\\ |\\ O\end{matrix}$, the presence of which could not explain the observed powerful exaltations; it is consonant with the structure $:C:NR:O$, experimental evidence for which has been adduced by Semper and Lichtenstadt (A., 1918, i, 437) and by Staudinger (A., 1919, i, 584).

The optical properties of the carbamidoximes (cf. Conduché, A., 1908, i, 12, 154), of the *aci*-forms of the nitroparaffins and of tetranitromethane are in agreement with the constitutions, $RR'C:N(:O)\cdot CO\cdot NH_2$, $RR'C:N(:O)\cdot OH$, and $(NO_2)_2C:N(:O)\cdot O\cdot NO_2$, respectively.

The physical constants have been observed partly with homogeneous material, partly with substances dissolved in quinoline which is found to be a very suitable solvent for this purpose. The following data, amongst others, are recorded. Heptaldoxime, $d_4^{99\cdot8}$ 0·8219, $n_{He}^{99\cdot8}$ 1·41514. α-Mesityl oxideoxime, b. p. 84°/11 mm., d_4^{100} 0·876, n_{He}^{100} 1·450. β-Mesityl oxideoxime, b. p. 95°/11 mm., d_4^{100} 0·881, n_{He}^{100} 1·462. α-Mesityl oxideoxime acetate, b. p. 101°/11 mm., d_4^{20} 0·986, n_{He}^{20} 1·474. β-Mesityl oxideoxime acetate, b. p. 107°/14 mm., d_4^{20} 0·990, n_{He}^{20} 1·478. α-Mesityl oxideoxime benzyl ether, b. p. 131°/11 mm., d_4^{20} 0·987, n_{He}^{20} 1·533. α-Benzaldoxime, m. p. 35°, d_4^{20} 1·110, n_{He}^{20} 1·593. α-Benzaldoxime *O*-methyl ether, b. p. 79°/11 mm., d_4^{20} 1·020, n_{He}^{20} 1·548. β-*Benzaldoxime* O-*methyl ether*, b. p. 79°/11 mm., d_4^{20} 1·028, n_{He}^{20} 1·550. α-Benzaldoxime acetate, d_4^{20} 1·107, n_{He}^{20} 1·544.

Heptaldoxime *N*-benzyl ether, $d_4^{99\cdot6}$ 0·9293, $n_{He}^{99\cdot6}$ 1·49714. Furfuraldoxime *N*-methyl ether, $d_4^{99\cdot8}$ 1·1185, $n_{He}^{99\cdot8}$ 1·56351. Furfuraldoxime *N*-benzyl ether, $d_4^{99\cdot7}$ 1·1270, $n_{He}^{99\cdot7}$ 1·59871. β-Benzaldoxime *N*-methyl ether, $d_4^{99\cdot9}$ 1·0528, $n_{He}^{99\cdot9}$ 1·59189. o-*Chlorobenzaldoxime* N-*phenyl ether*, coarse, pale yellow crystals, m. p. 81·5—82·5° (from *o*-chlorobenzaldehyde and phenylhydroxylamine), $d_4^{100\cdot3}$ 1·2008, $n_{He}^{100\cdot3}$ 1·64853. Phenylnitromethane, $d_4^{24\cdot7}$ 1·1540, $n_{He}^{24\cdot7}$ 1·52850. aci-*Phenylnitromethane methyl ether*, from nitromethane, methyl sulphate, and sodium hydroxide, a pale yellow liquid with an odour of bitter almonds, b. p. 117°/15 mm., ca. 83°/1·5 mm., $d_4^{15\cdot0}$ 1·1241, $n_{He}^{15\cdot0}$ 1·58708. Tetranitromethane, $d_4^{16\cdot9}$ 1·6425, $n_{He}^{16\cdot9}$ 1·43976.

Benzylidenemethylamine, $CHPh{:}NMe$, b. p. 185°, d_4^{20} 0·962, n_{He}^{20} 1·553. Benzylidene-ethylamine, b. p. 195°, d_4^{20} 0·937, n_{He}^{20} 1·541. Benzylidene*iso*amylamine, b. p. 245°, d_4^{20} 0·906, n_{He}^{20} 1·519. Benzylideneaniline, b. p. 300°, $d_4^{99\cdot3}$ 1·0041, $n_{He}^{99\cdot3}$ 1·61041. Benzylidene-*o*-toluidine, b. p. 314°, d_4^{20} 1·041, n_{He}^{20} 1·635. H. W.

Reactions of Cinnamalphenylnitrone. D. Bigiavi and M. Marri (*Gazzetta*, 1924, **54**, 99—113).—Among the products obtained by Weitnauer (Dissertation, Basle, 1904) on reducing phenyl*iso*cinnamaldoxime by means of sodium or sodium amalgam and absolute alcohol were two compounds described by this author as (1) liquid secondary base, b. p. 190—190·5°/8 mm., and (2) solid secondary base, m. p. 90—90·5°, and regarded as having the structures, $NHPh{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Ph$, and $NHPh{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2Ph$, respectively. The authors show that the solid base, m. p. 90°, is actually hydrocinnamanilide, its formation being the result of migration of the oxygen atom of the phenyl*iso*cinnamaldoxime from the nitrogen to the adjacent carbon atom, followed by hydrogenation of the cinnamanilide thus formed: $O{:}NPh{:}CH{\cdot}CH{:}CHPh \longrightarrow NHPh{\cdot}CO{\cdot}CH{:}CHPh \longrightarrow NHPh{\cdot}CO{\cdot}CH_2{\cdot}CH_2Ph$. Similar transpositions are exhibited by a large number of compounds, including nitrones (cf. Miescher, "Nitrone und Nitrene," Zurich, 1918, 20). By acetic anhydride, cinnamalphenylnitrone is converted quantitatively into the acetyl derivative of cinnamanilide as the result of an intensely exothermic reaction, hydrolysis then yielding the anilide: $O{:}NPh{:}CH{\cdot}CH{:}CHPh \longrightarrow NHPh{\cdot}CO{\cdot}CH{:}CHPh$; catalytic reduction of cinnamanilide by means of hydrogen and platinum black yields hydrocinnamanilide, identical with the product obtained by heating aniline with hydrocinnamic acid.

By catalytic reduction, Cusmano (A., 1922, i, 143) has converted nitrones into hydroxylamines. From cinnamalphenylnitrone this author has obtained, by reduction with hydrogen and platinum black, a compound which is apparently a hydroxylamine. This marked divergence in behaviour must be due to the presence of conjugated double bonds in the molecule of cinnamalphenylnitrone.

By dilute sulphuric acid, cinnamalphenylnitrone is readily converted into the Schiff's base of *p*-aminophenol:

$$O{:}NPh{:}CH{\cdot}CH{:}CHPh \longrightarrow OH{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}CH{:}CHPh$$

(cf. Angeli, Alessandri, and Pegna, A., 1910, i, 552). Analogous reactions produced by dilute sulphuric acid are: $O{:}NH_2Ph \longrightarrow OH{\cdot}C_6H_4{\cdot}NH_2$; $O{:}NPh{:}NPh \longrightarrow OH{\cdot}C_6H_4{\cdot}N{:}NPh$; $O{:}NPhMe_2$

$\longrightarrow$ $OH\cdot C_6H_4\cdot NMe_2$. On other nitrones, the acid exerts a hydrolysing action, the original aldehyde or ketone and aryhydroxylamine being regenerated.

The *acetyl* derivative of cinnamanilide, $C_{17}H_{15}O_2N$, forms acicular crystals, m. p. 138—139°.

Hydrocinnamanilide, $C_{15}H_{15}ON$, crystallises in lustrous, white needles, m. p. 98°, and exhibits the normal molecular weight in acetic acid. It is stable towards alcoholic potassium hydroxide, but is rapidly hydrolysed when heated with dilute sulphuric acid. Sodium and alcohol reduce it to aniline and another base, which is probably Weitnauer's liquid secondary base. With nitrous acid, it appears to yield a nitrosoamine. Its *acetyl* derivative, $C_{17}H_{17}O_2N$, forms minute, refractive crystals, m. p. 45°. T. H. P.

Oxides of the Stereoisomeric Trithiobenzaldehydes. O. HINSBERG (*Ber.*, 1924, **57**, [*B*], 417—419).—A detailed reply to the criticisms of Fromm and Schultis (A., 1923, i, 580) on the author's work (A., 1914, i, 185). Contrary to the views of Fromm and Schultis, α-trithiobenzaldehyde pentoxide (disulphone-sulphoxide) must be regarded as a homogeneous substance. The individuality of δ-trithiobenzaldehyde tetroxide is not, however, established with equal certainty, and it is possible that the product is a difficultly separable mixture of the tri-, tetra-, and pent-oxides, but this is not conclusively proved by the experiments of Fromm and Schultis. Valid evidence against the existence of δ-trithiobenzaldehyde has not been adduced. H. W.

Pinacolin Transformation in the Dehydration of 1 : 2-Dimethyl*cyclo*hexane-1 : 2-diol. S. NAMETKIN and N. DELEKTORSKY (*Ber.*, 1924, **57**, [*B*], 583—587).—1 : 2-Dimethyl*cyclo*hexane-1 : 2-diol, m. p. 92—93°, prepared by hydrating the corresponding oxide at the ordinary temperature with very dilute sulphuric acid, was heated at 150—160° for 3 hours with acidulated water. On cooling, the pinacolin separated as an oil possessing a peppermint-like odour and distilling, after purification by means of its semicarbazone, at 60·5°/20 mm. It was found to be identical with 1-methyl-1-*cyclo*pentyl methyl ketone (Meerwein, A., 1919, i, 162). The pinacolin transformation is therefore accompanied by the change from a six-ring to a five-ring. The reverse change occurs on dehydrating 1-methyl-1-α-hydroxyethyl*cyclo*pentane, the product being 1 : 2-dimethyl-Δ^1-*cyclo*hexene (Meerwein, *loc. cit.*). F. A. M.

Oxidation of Sabinene with Chromyl Chloride. A Correction. G. G. HENDERSON and J. M. ROBERTSON (*J. Chem. Soc.*, 1924, **125**, 765—766).—The supposed 4-*iso*propylidene*cyclo*hexanone obtained by the oxidation of sabinene with chromyl chloride (*Chem. Soc. Trans.*, 1922, **121**, 2717) has now been found to be *p*-tolyl methyl ketone. The alcohol obtained by its reduction is therefore *p*-tolylmethylcarbinol. The formation of this ketone from sabinene is attributed to oxidation of part of the sabinene to cymene, which with chromyl chloride forms the compound $C_{10}H_{14},2CrO_2Cl_2$, from which *p*-tolyl methyl ketone is formed on decomposition with water. R. B.

Change of State of Aggregation and Polymorphism. III. Polymorphism of Benzophenone. K. Schaum and K. Unger (*Z. anorg. Chem.*, 1924, **132**, 90—98; cf. A., 1916, i, 405).—The instability of the metastable form of benzophenone makes the investigation of its pseudo-binary character difficult. On this account, the *p*-halogen and *p*-hydroxy derivatives were examined. These were found to be monotropic trimorphic, but the m. p. of the three forms lie very close together, not more than 0·5° apart. The effect of previous history on the m. p. of benzophenone was examined. No difference could be detected after heating for different periods of time at different temperatures. H. T.

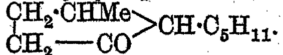
Preparation of 3 : 3′-Dinitrobenzophenone. E. de B. Barnett and M. A. Matthews (*J. Chem. Soc.*, 1924, **125**, 767).—By nitration of benzophenone in sulphuric acid solution with nitric acid (*d* 1·50) at 25—30°, a yield of 50% of theory of crude 3 : 3′-dinitrobenzophenone was obtained, which after one crystallisation from methyl ethyl ketone melted at 155°. R. B.

Valency. I. Estimation of the Strength of the Bond between a Radical and Carbon. A. Schonberg, R. Abelsdorff, H. Kirchrath, W. Malchow, and A. Rosenbach (*Annalen*, 1924, **436**, 205—218).—The reaction between benzophenone and sodamide, first studied by Haller (A., 1908, i, 987), has been applied to substituted aromatic ketones. Benzophenone, in toluene solution, gives as a final product benzamide: $Ph_2CO+NaNH_2 \longrightarrow Ph_2C(NH_2)ONa \longrightarrow C_6H_6+Ph{\cdot}CO{\cdot}NHNa \longrightarrow Ph{\cdot}CO{\cdot}NH_2$. With an unsymmetrical substituted benzophenone, the reaction may proceed in two ways, giving benzene and a substituted benzamide, or a substituted benzene and benzamide. It is shown that Haller's explanation (*loc. cit.*) of the reaction is incorrect; for instance, diphenyl phenyl ketone with sodamide in toluene solution gives diphenyl, which agrees with the above scheme. The yields in this reaction are practically quantitative, so that by determining the proportions of the free acids (obtained by hydrolysis of the amides) formed, it is possible to determine the relative affinity of the various radicals for carbonyl carbon, and comparative numerical values can be assigned to each radical. Taking the affinity of the phenyl radical as the unit, the following values are assigned to substituted phenyl radicals containing the substituent groups indicated:—*m*-chloro-, 0·05—0·32; *m*-bromo-, 0·08—0·38; *p*-chloro-, 0·18—0·51; *p*-bromo-, 0·18—0·65; *p*-methoxy-, 1·12—2·16; and *p*-dimethylamino-, about 1·23. The value for the radicals CPh_3– and $CPh_2(ONa)$– is less than 0·14. If the ketone is not decomposed by sodamide, for example, phenyl triphenylmethyl ketone, hydrolysis with alkali is resorted to, the final products being triphenylacetic acid and benzoic acid, in proportions depending on the relative affinities of the triphenylmethyl and phenyl radicals. The method fails with aliphatic ketones, a sodium compound of the ketone being formed.

p-*Methylmercaptobenzophenone*, colourless prisms, m. p. 79°, was synthesised from benzoyl chloride, methyl phenyl sulphide, and aluminium chloride in carbon disulphide solution; (*phenylhydrazone*, colourless crystals, m. p. 90°). p-*Methylmercaptobenzoic acid*, by the action of sodamide on the ketone in toluene solution, forms prisms, m. p. 192°. 4 : 4′-Dimethylmercaptobenzophenone, from thioanisole and oxalyl chloride in presence of aluminium chloride in ice-cold carbon disulphide solution, forms colourless scales, m. p. 125·5° (anil, yellow prisms, m. p. 135°). A. E. C.

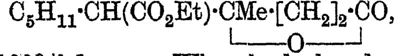
Isomeric *p*′-Methylchalkones [*p*-Tolyl Styryl Ketones]. C. Weygand (*Ber.*, 1924, **57**, [*B*], 413—417).—*p*-Tolyl methyl ketone, condensed with benzaldehyde and sodium ethoxide, yields *p*-methylchalkone (*p*-tolyl styryl ketone), m. p. 590 (cf. Sorge, A., 1902, i, 379); on recrystallising several months later, it was suddenly converted into the isomeric form, m. p. 77°, described by Kostanecki (A., 1896, i, 688), and during the night all the other uncovered preparations were converted into the same modification. All subsequent preparations gave only the 77° form, which on heating to 135° and cooling deposits the form, m. p. 59°; this is at once changed into the 77° modification when touched with a crystal of the latter. Both forms could be crystallised from suitable solvents at first, but once the 77° form had appeared it became nearly impossible to recover the 59° form from solution except by working at low temperatures or in air-tight vessels. Both forms give orange-yellow solutions in concentrated sulphuric acid, the 77° form being deposited on dilution; both yield the same *dibromide* as a white, crystalline powder, m. p. 175—176°, the same *compound* with stannic chloride, m. p. 85° (not sharp), and the same aniline additive *compound*, m. p. 141°. At 21°, 100 g. of benzene dissolve about 55·8 g. of the 77° form, and 166·8 g. of the 59° form. Both forms have normal molecular weights in benzene. F. A. M.

Insecticides. IV. Constitution of Tetrahydropyrethrone. H. Staudinger and L. Ruzicka (*Helv. Chim. Acta*, 1924, **7**, 236—244).—It was shown in a previous paper (p. 523) that reduction of pyrethrolone by the Paal–Skita method gives tetrahydropyrethrolone. When the reduction is pushed to the limit, the hydroxyl group is also reduced, tetrahydropyrethrone being formed. Complete reduction is effected more readily with the acetate or the methyl ether than with pyrethrolone itself. *Tetrahydropyrethrone* is a colourless, mobile liquid with a faint, ethereal odour, b. p. 100—101°/12 mm. Its constitution, determined from its oxidation products, is 3-*methyl*-2-n-*amylcyclopentanone*,



$$\left.\begin{array}{l}\mathrm{CH_2{\cdot}CHMe}\\ \mathrm{CH_2{-}{-}CO}\end{array}\right>\mathrm{CH{\cdot}C_5H_{11}}.$$

The *semicarbazone* varies in melting point from 160° to 194°, according to the manner in which the ketone is prepared. That of m. p. 194°, from the ketone obtained by reduction of pyrethrolone acetate, is the *lævo* form; that having m. p. 160° is the *racemic* form. The p-*nitrophenylhydrazone* (*r*-form) forms yellow needles, m. p. 87°. By oxidation of tetrahydropyrethrone with potassium permanganate, hexoic and lævulic acids were obtained. Their formation is compatible with two possible formulæ, a *cyclo*pentane derivative with the keto group in the ring or a *cyclo*butane derivative with the keto group in the side chain. The oxime of the former should give a lactam by the Beckmann change, whilst the oxime of the latter should give an acid amide. The *oxime* of tetrahydropyrethrone is a colourless oil, b. p. 84—85°/0·1 mm., which, by treatment with concentrated sulphuric acid, is converted into the iso-*oxime*, a viscous oil, b. p. 120°/0·1 mm. The latter is converted by boiling hydrochloric acid into *δ-amino-γ-methyldecoic acid*, which by treatment with nitrous acid is converted into the *lactone* of *δ-hydroxy-γ-methyldecoic acid*. The constitution of tetrahydropyrethrone as 3-methyl-2-*n*-amyl*cyclo*pentanone is therefore established. E. H. R.

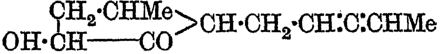
Insecticides. V. Synthesis of Tetrahydropyrethrone, the Reduction Product of Pyrethrolone. H. Staudinger and L. Ruzicka (*Helv. Chim. Acta*, 1924, 7, 245—259).—The constitution of tetrahydropyrethrone, which was concluded to be 3-methyl-2-*n*-amyl*cyclo*pentanone (preceding abstract), has been confirmed by synthesis as follows: *Ethyl α-bromoheptoate* (colourless oil, b. p. 106—107°/12 mm.) was condensed with ethyl lævulate, forming the *γ-lactone* of *ethyl hydrogen γ-hydroxy-γ-methylnonane-αδ-dicarboxylate*,  $C_5H_{11}\cdot CH(CO_2Et)\cdot \underbrace{CMe\cdot[CH_2]_2\cdot CO}_{O}$, a colourless, viscous oil, b. p. 130°/0·1 mm. When hydrolysed with 25% potassium hydroxide, the lactone ester is decomposed to a great extent into heptoic and lævulic acids, and only a small yield of *γ-hydroxy-β-methylnonane-αδ-dicarboxylic acid lactone* is obtained, white crystals, m. p. 86—87°. When the disodium salt of the free adipic acid is heated, it loses water and carbon dioxide, forming *γ-methyl-Δ^{γ}-decenoic acid*, $C_5H_{11}\cdot CH\colon CMe\cdot[CH_2]_2\cdot CO_2H$, a viscous oil of peculiar odour, b. p. 160—163°/15 mm. (p-*toluidide*, m. p. 44—45°; *α-naphthylamide*, m. p. 63—64°), which is reduced by the Paal–Skita method to *γ-methyldecoic acid*, a colourless oil, b. p. 150—152°/12 mm. (p-*toluidide*, m. p. 34—36°; *α-naphthylamide*, m. p. 61—62°).

When the condensation of ethyl α-bromoheptoate and ethyl lævulate with zinc was continued for a prolonged period at 150°, one of the reaction products was a butylene derivative, *ethyl hydrogen γ-methyl-Δ^{γ}-nonylene-αδ-dicarboxylate* (*δ-carbethoxy-γ-methyl-Δ^{γ}-decenoic acid*), $C_5H_{11}\cdot C(CO_2Et)\colon CMe\cdot[CH_2]_2\cdot CO_2H$, a colourless oil, b. p. 150°/0·4 mm., which could not be reduced with hydrogen (Paal–Skita) or sodium amalgam; the *ethyl* ester has b. p 170—180°/15 mm. When the ester was boiled with sodium and xylene, and the sodium compound of the resulting methylamyl*cyclo*pentanonecarboxylate boiled with 20% sulphuric acid, *3-methyl-2-amyl-Δ^2-*cyclo*pentenone* was obtained, a colourless oil, b. p. 115—117°/12 mm. (*semicarbazone*, m. p. 175—176°; p-*nitrophenylhydrazone*, m. p. 118—119°). The unsaturated ketone could only be reduced by passing its vapour with hydrogen over nickel at 240—250°. The resulting 3-methyl-2-amyl*cyclo*pentanone was identical with tetrahydropyrethrone.

The following compounds were obtained in unsuccessful attempts to effect the synthesis: 3-*Methyl*-5-n-*amyl*cyclo*pentanone*, colourless liquid, b. p. 107—109°/14 mm. (*semicarbazone*, m. p. 147—148°; p-*nitrophenylhydrazone*, m. p. 134—135°), by condensing ethyl β-methyladipate to a *cyclo*pentanonecarboxylic acid by Dieckmann's method (A., 1900, i, 297) and heating the sodium salt of this acid with amyl bromide. *Ethyl* β-*methylbutane*-ααδ-*tricarboxylate*, colourless oil, b. p. 135°/0·4 mm. (from ethyl malonate and ethyl γ-bromovalerate, in presence of sodium), reacted slowly with *n*-amyl bromide in presence of alcoholic sodium ethoxide, giving the same methylamyl*cyclo*pentanone as above and by-products.

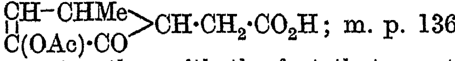
E. H. R.

Insecticides. III. Constitution of Pyrethrolone. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 212—235).—The alcoholic constituent of the active substances in insect powder, pyrethrolone, $C_{11}H_{16}O_2$, is obtained from the semicarbazone already described by careful cold hydrolysis with potassium hydrogen sulphate in presence of benzene and water. It forms a viscous oil, b. p. 111—112°/0·05 mm., $[\alpha]_D^{20}$ −6·2° (approx.). Pyrethrolone probably has the constitution 1-*methyl*-2-*pentadienyl*-cyclo*pentane*-4-*ol*-3-*one*,



$$\begin{array}{l}CH_2\cdot CHMe\\ \quad|\\ OH\cdot CH——CO\end{array}\!\!>CH\cdot CH_2\cdot CH{:}C{:}CHMe$$

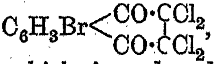
; it forms a p-*nitrophenylosazone*, a brown, microcrystalline powder, decomposing above 350°; and an *acetate*, $C_{13}H_{18}O_3$, a colourless, mobile oil, b. p. 104—105°/0·5 mm., $[\alpha]_D^{15}$ −23·79°, which forms a crystalline *semicarbazone*, m. p. 143—145°. When treated with alkali it undergoes autoxidation, forming *dehydropyrethrolone*, a mobile oil, b. p. 82°/0·05 mm., which gives a *semicarbazone*, m. p. 251°, and a second oxidation product, a viscous oil, probably a polymerised form of the first; both are weakly acidic. By methylation with methyl alcohol and concentrated sulphuric acid, pyrethrolone semicarbazone forms a *methyl* ether, m. p. 183°, which, by removal of the semicarbazone group gives the *methyl* ether of pyrethrolone, a mobile oil, b. p. 82—83°/0·25 mm. Pyrethrolone itself can be methylated with methyl sulphate to give the same product, but with methyl alcohol and sulphuric acid it gives a different product forming a *semicarbazone*, m. p. 207°. The *ethyl* ether of pyrethrolone is a colourless liquid, b. p. 102—103° in the highest vacuum; *semicarbazone*, m. p. 179—180°.

When pyrethrolone is reduced by the Paal–Skita method, it takes up 2 mols. of hydrogen, forming *tetrahydropyrethrolone*, which is shown (p. 521) to be 1-*methyl*-2-n-*amyl*cyclo*pentane*-4-*ol*-3-*one*; it is a viscous oil, b. p. 160—162°/10 mm., 108—110°/0·1 mm.; $[\alpha]_D^{20}$ −11·32°, with strong reducing properties. When esterified with chrysanthemumyl chloride, it gives a product having no insecticidal properties. Tetrahydropyrethrolone forms a p-*nitrophenylosazone*, decomposing above 350°; a *semicarbazone*, m. p. 189—190° (decomp.); an *acetate*, a mobile oil, b. p. 110°/0·16 mm., and a *methyl* ether, a colourless, mobile oil, b. p. 128°/12 mm., obtained by reduction of pyrethrolone methyl ether. By oxidation with potassium permanganate, tetrahydropyrethrolone gives hexoic acid. Decomposition of the mono-ozonide of pyrethrolone gives acetaldehyde and acetic acid, showing the presence of an ethylidene group. Malonic acid was also obtained by further oxidising the products obtained from the ozonide with hydrogen peroxide. By ozonisation of pyrethrolone acetate, an acid was obtained which appeared to be an *acetoxymethyl*cyclo*pentenone-homocarboxylic acid*,  $\left.\begin{array}{l}\mathrm{CH{-}CHMe}\\ \|\\ \mathrm{C(OAc)\cdot CO}\end{array}\right>\mathrm{CH\cdot CH_2\cdot CO_2H}$; m. p. 136—138°. The above observations, together with the fact that pyrethrolone only absorbs 1 mol. of bromine with ease, support the view that the side chain contains the allene grouping, although this grouping has not previously been found in a natural product. E. H. R.

Hydroxyhydrindone and Chromanone. F. Mayer and L. van Zütphen (*Ber.*, 1924, **57**, [*B*], 618).—A correction. In a previous paper (this vol., i, 410) the authors claimed to have synthesised chromanone by the action of aluminium chloride on *o*-hydroxyphenyl β-chloroethyl ketone. The product is now admitted to be 7-hydroxyhydrindone, b. p. 128°/13 mm. The benzylidene compound is coloured yellow by sodium hydroxide solution, but is not dissolved even on boiling. (Cf. Krollpfeiffer and Schultze, following abstract.) F. A. M.

Formation of Hydroxyhydrindones from Phenyl Esters of β-Halogenpropionic Acids by Heating with Aluminium Chloride. F. Krollpfeiffer and H. Schultze (*Ber.*, 1924, **57**, [*B*], 600—601; cf. this vol., i, 411).—p-*Tolyl* β-*bromopropionate* is obtained in quantitative yield by heating *p*-cresol with β-propionyl chloride and is a colourless oil, b. p. 162°/14 mm. When it is heated with twice its weight of aluminium chloride at 100—120°, and the product decomposed with iced hydrochloric acid, 80% of the theoretical yield of 1-*hydroxy*-4-*tolyl* β-*bromoethyl ketone* is obtained, forming small, colourless plates, m. p. 72—73°. At 160—170° the product is 4-methyl-7-hydroxyhydrindone, m. p. 110—111°, the yield being 60% of theory. This provides strong evidence that the "γ-chromanone" obtained by Mayer and van Zütphen (this vol., i, 410) is really 7-hydroxyhydrindone. (Cf. Mayer and Zütphen, preceding abstract.) F. A. M.

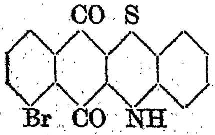
Synthesis of *m*-Dimethoxyphenyl Ethyl and Methyl Ketones. F. Mauthner (*J. pr. Chem.*, 1924, [ii], **107**, 103—108).—To obtain better yields of 3 : 5-dimethoxyphenyl ethyl ketone than were obtained from 3 : 5-dimethoxybenzoyl chloride and zinc ethyl iodide (A., 1922, i, 457), methyl 3 : 5-dimethoxybenzoate was condensed with ethyl acetate by the Claisen method and the *ethyl* 3 : 5-*dimethoxybenzoylacetate*, a pale yellow oil (*pyrazolone* derivative with phenylhydrazine, m. p. 153—154°), was converted by treatment with methyl iodide and sodium ethoxide, followed by hydrolysis with 25% sulphuric acid, into 3 : 5-dimethoxyphenyl ethyl ketone, colourless needles, m. p. 34—35° (*semicarbazone*, colourless needles, m. p. 130—131°). Hydrolysis of ethyl 3 : 5-dimethoxybenzoylacetate with 25% sulphuric acid yields 3 : 5-*dimethoxyphenyl methyl ketone*, colourless needles, m. p. 42—43°, b. p. 151—152°/10 mm. (p-*nitrophenylhydrazone*, reddish-yellow needles, m. p. 157—158°; *semicarbazone*, colourless needles, m. p. 186—187°). Condensation of 3 : 5-dimethoxybenzaldehyde and sodium propionate by the Perkin reaction gives 3 : 5-*dimethoxy-α-methylcinnamic acid*, colourless needles, m. p. 153—154°, but attempts to convert this into 3 : 5-dimethoxypropenylbenzene through loss of carbon dioxide failed. 3 : 5-*Dimethoxyphenylethylcarbinol*, b. p. 170—171°/12 mm. (*phenylurethane*, colourless plates, m. p. 86—87°), was obtained by the Grignard reaction from 3 : 5-dimethoxybenzaldehyde and ethyl iodide; with excess of Grignard reagent 3 : 5-*dimethoxypropenylbenzene* was formed but rapidly polymerised. R. B.

Quinones of Linear Ring Systems with Reactive Halogen in the Non-quinonoid Nucleus. K. Fries and E. Köhler (*Ber.*, 1924, 57, [*B*], 496—510).—A continuation of previous work (Fries and Kerkow, A., 1922, i, 577). 5-Bromoacetnaphthalide can be prepared by the reduction of 5-bromo-1-nitronaphthalene with iron filings and acetic acid or with zinc dust and ammonium chloride and subsequent acetylation of the product or, more economically, by means of iron powder and glacial acetic acid and subsequent treatment of the solution with acetic anhydride. It is converted by a mixture of glacial acetic acid and nitric acid (*d* 1·48) at —2° into a mixture of 5-bromo-2-nitroacetonaphthalide and 5-bromo-4-nitroacetonaphthalide (m. p. 225°), which can be only incompletely separated by fractional crystallisation. Treatment of the mixture with aqueous-alcoholic sodium hydroxide solution leads to the ready isolation of 5-*bromo*-4-*nitro*-α-*naphthylamine*, reddish-brown needles or prismatic crystals, m. p. 192° (*monoacetate*, pale yellow, lustrous needles, m. p. 225°; *diacetate*, pale brown leaflets, m. p. 170°), and 5-*bromo*-2-*nitroacetonaphthalide*, m. p. 240°. 5-Bromo-4-nitro-α-naphthylamine is reduced by stannous chloride and hydrochloric acid in glacial acetic acid solution to 5-*bromo*-1 : 4-*naphthylenediamine*, slender, pale green needles, m. p. 132° (*dihydrochloride*, slender, colourless needles; *diacetyl* compound, colourless needles, m. p. 257°). 5-*Bromo*-1 : 4-*naphthaquinone*, golden-yellow prisms, m. p. 160°, and 5-*bromo*-2-*anilino*-1 : 4-*naphthaquinone*, red, prismatic leaflets, m. p. 219°, are described. The diamine hydrochloride (or the stannic double salt) is transformed by exhaustive chlorination in the presence of glacial acetic and concentrated hydrochloric acids into 2 : 2 : 3 : 3-*tetrachloro*-5-*bromo*-1 : 4-*diketo*-1 : 2 : 3 : 4-*tetrahydronaphthalene*,  $C_6H_3Br<\begin{matrix}CO\cdot CCl_2\\ | \\ CO\cdot CCl_2\end{matrix}$, needles or monoclinic crystals, m. p. 120°, which is reduced by stannous chloride to 2 : 3-*dichloro*-5-*bromo*-1 : 4-*dihydroxynaphthalene*, colourless needles, m. p. 196° (*acetate*, needles, m. p. 154°). The latter substance is oxidised by ferric chloride to 2 : 3-*dichloro*-5-*bromo*-1 : 4-*naphthaquinone*, pale yellow, prismatic crystals, m. p. 180°, which, with aniline, gives 3-*chloro*-5-*bromo*-2-*anilino*-1 : 4-*naphtha*-

quinone, dark red needles, m. p. 239° (the assumption that the chlorine atom in position 2 suffers replacement is arbitrary).

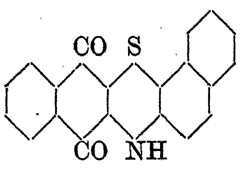
[With G. SCHÜRMANN.]—A similar sequence of changes starting from 8-chloro-4-nitro-α-acetnaphthalide (which is the main product of the nitration of 8-chloro-α-acetnaphthalide) leads to the production of 5-chloro-1 : 4-naphthaquinone and its derivatives. The following compounds are described: 8-*Chloro*-4-*nitro*-α-*naphthylamine*, brownish-red, lustrous plates, m. p. 203° (*acetyl* derivative, needles, m. p. 167°); 5-*chloro*-1 : 4-*naphthylenediamine*, slender, pale yellow needles, m. p. about 116° (decomp.) (*diacetyl* derivative, slender, colourless needles, m. p. 269°); 5-*chloro*-1 : 4-*naphthaquinone*, yellow needles, m. p. 163°; 5-*chloro*-2-*anilino*-1 : 4-*naphthaquinone*, red needles with a bronzy lustre, m. p. 219°; 2 : 2 : 3 : 3 : 5-*pentachloro*-1 : 4-*dihydroxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, colourless leaflets, m. p. (indefinite) 82°; 2 : 3 : 5-*trichloro*-1 : 4-*dihydroxynaphthalene*, colourless needles, m. p. 204° (*acetate*, needles, m. p. 162°); 2 : 3 : 5-*trichloro*-1 : 4-*naphthaquinone*, coarse yellow needles, m. p. 156°; 3 : 5-*dichloro*-2-*anilino*-1 : 4-*naphthaquinone*, dark red needles, m. p. 225°; 3-*chloro*-2 : 5-*dianilino*-1 : 4-*naphthaquinone*, needles, m. p. 221°.

5-*Bromo*-2-*nitro*-α-*naphthylamine*, orange-red needles, m. p. 223°, is obtained by hydrolysing the corresponding monoacetyl derivative (see above) with sulphuric acid (*diacetyl* derivative, m. p. 133°). The acetyl compound is converted by boiling, 2*N*-sodium hydroxide solution into 5-*bromo*-2-*nitro*-α-*naphthol*, golden-yellow leaflets, m. p. 142°. 5-*Bromo*-1 : 2-*naphthylenediamine*, colourless plates or slender needles, m. p. 122°, is obtained by reduction of the nitro-amine with tin and hydrochloric acid; the corresponding *diacetyl* derivative, prismatic crystals, m. p. 287°, is transformed by boiling alcoholic sodium hydroxide solution into 6-bromo-2-methyl-αβ-naphthiminazole, colourless, slender needles, m. p. 242°, which is also obtained by the reduction of 5-bromo-2-nitro-α-naphthylamine with stannous chloride in glacial acetic acid solution. The diamine condenses with benzil in alcoholic solution to form the *quinoxaline* derivative, $C_{24}H_{15}N_2Br$, pale yellow needles, m. p. 214°. 3 : 5-*Dichloro*-5-*bromo*-1 : 2-*diketo*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (obtained by chlorination of the diamine), apparently monoclinic crystals, m. p. 93°, 3-*chloro*-5-*bromo*-1 : 2-*dihydroxynaphthalene*, colourless needles, m. p. 176° (*diacetyl* derivative, coarse crystals, m. p. 147°), and 3-*chloro*-5-*bromo*-1 : 2-*naphthaquinone*, small, red plates, m. p. 177°, are described.



3-*Chloro*-5-*bromo*-2-*anilino*-1 : 4-*naphthaquinone*, dark red needles, m. p. 239°, is converted by treatment with sodium sulphide and oxidation of the product by air into 7-*bromo*-ββ-*naphthaphenthiazine*-6 : 11-*quinone* (annexed formula), bluish-green, prismatic crystals, m. p. 325°; the corresponding *sulphoxide*, brownish-red, coarse crystals, m. p. 270°, and the *sulphone*, orange-red, lustrous leaflets, m. p. above 360°, are described. Boiling acetic anhydride and zinc dust convert the quinone into the *triacetyl* derivative of 7-*bromo*-6 : 11-*dihydroxy*-

ββ-*naphthaphenthiazine*, lustrous leaflets, m. p. 299°. 7-*Anilino-ββ-naphthaphenthiazine*-6 : 11-*quinone* crystallises in slender, dark violet needles, m. p. 265°; it gives a yellow vat with hyposulphite. 7-p-*Anisidino*-ββ-*naphthaphenthiazine*-6 : 11-*quinone* forms dark violet crystals, m. p. 230°.



3-*Chloro*-2-β-*naphthylamino*-1 : 4-*naphthaquinone*, m. p. 194°, prepared from 2 : 3-dichloro-1 : 4-naphthaquinone and β-naphthylamine, is transformed in the usual manner into 1 : 2-*benzo*-ββ-*naphthaphenthiazine*-6 : 11-*quinone* (annexed formula), dark, greenish-blue, prismatic crystals, m. p. 300°; the corresponding sulphone crystallises in orange-red leaflets, m. p. above 400°. Zinc dust and boiling acetic anhydride transform the quinone into the *triacetyl* derivative of 6 : 11-*dihydroxy*-1 : 2-*benzo*-ββ-*naphthaphenthiazine*, colourless crystals, m. p. 217°. H. W.

Reduction Products of the Hydroxyanthraquinones. V. F. L. GOODALL and A. G. PERKIN (*J. Chem. Soc.*, 1924, **125**, 470—476).—Hydroxyanthranols can be readily prepared in excellent yield by digesting hydroxyanthraquinones with a boiling 20% solution of stannous chloride in 33% hydrochloric acid. The method is serviceable only in those cases in which anthranol formation has been effected by other methods. With purpurin and purpuroxanthin, reduction is incomplete, whilst quinizarin yields quantitatively deep orange-red crystals of 1 : 4 : 9-trihydroxyanthrone, m. p. 152—154° (A., 1920, i, 745).

The following anthranols have been obtained by this method: 1- and 3-hydroxy-, 3 : 6-, 3 : 7-, and 4 : 8-dihydroxy-anthranols, anthrapurpurin anthranol, and anthragallol anthranol. Deoxyalizarin (3 : 4-dihydroxyanthranol), when acetylated and oxidised with ferric chloride, yields 3 : 4 : 5′ : 6′-*tetrahydroxydianthrone*, small, yellow needles, m. p. 268—270° (decomp.); *hexa-acetyl* derivative, $C_{40}H_{30}O_{12}$, colourless needles, m. p. 236—238°. With alcoholic sulphuric acid, it gives *dihydroxy*-3 : 6′-*diethoxydianthrone*, $C_{32}H_{22}O_6$, small plates, m. p. 271—274°, which on careful oxidation with chromic acid yields alizarin β-ethyl ether, orange needles, m. p. 188—189°. *Tetra-acetyldiethoxydianthranol* has m. p. 248—250°. By treatment with methyl sulphate and alkali the dihydroxydiethoxydianthrone is converted into 3 : 4 : 5′ : 6′-*tetramethoxydianthrone*, colourless needles, m. p. 255—256°. Attempts to convert the tetrahydroxydianthrone into the corresponding helianthrone were unsuccessful. Both deoxyalizarin and tetrahydroxydianthrone are mordant dyes. With bromine in carbon disulphide solution, deoxyalizarin dimethyl ether is converted into 10-bromo-3 : 4-dimethoxyanthranol, from which by the action of dimethylamine or of alcoholic potassium hydroxide only alizarin dimethyl ether is obtained. Acetyldeoxyalizarin, on treatment with nitric acid in alcohol or acetic acid, yields 10-*nitro*-3 : 4-*dihydroxyanthranol diacetate*, $C_{18}H_{13}O_7N$, colourless needles, m. p. 156° (decomp.). The violet colour observed when nitric acid is added to a solution of deoxyalizarin in sulphuric acid is due to the production of nitrodihydroxyanthrone. R. B.

Derivatives of β-Methylanthraquinone. IV. Nitro Derivatives of β-Methylanthraquinone and some of their Transformation Products. R. Eder, C. Widmer, and R. Bütler (*Helv. Chim. Acta*, 1924, 7, 341—357).—The nitro-β-methylanthraquinone prepared by Römer and Link by nitration of β-methylanthraquinone (A., 1883, 1138) has been supposed to be 1-nitro-3-methylanthraquinone, on the ground that the hydroxymethylanthraquinone prepared from it, m. p. 177—178°, is identical with the 1-hydroxy-3-methylanthraquinone prepared synthetically by Bentley, Gardner, and Weizmann (T., 1907, **91**, 1626). Repetition of this work shows that the hydroxy compound from nitro-β-methylanthraquinone really has m. p. 181—182° and is identical with synthetic 1-hydroxy-2-methylanthraquinone. The nitro compound is therefore 1-nitro-2-methylanthraquinone. It is converted into α-aminoanthraquinone through the 1-aminoanthraquinone-2-carboxylic acid by boiling the latter with potassium stannite solution. The nitro compound is best prepared by Römer and Link's method; at higher temperatures, red by-products are formed.

Dinitration of β-methylanthraquinone or nitration of 1-nitro-2-methylanthraquinone gives a mixture of two isomerides, the 1 : 5- and 1 : 8-dinitro compounds. 1 : 5-*Dinitro-2-methylanthraquinone* forms yellow needles, m. p. 329—331°, subliming with partial decomposition in white needles; it is soluble in 50 parts of boiling pyridine, 450 of boiling acetic acid, very sparingly soluble in other solvents. By oxidation with chromic acid in boiling nitric acid solution it gives 1 : 5-*dinitroanthraquinone-2-carboxylic acid*, needles, m. p. 337—339°. By distillation of the *silver* salt (a red powder), 1 : 5-dinitroanthraquinone is obtained, m. p. above 350°, giving by reduction 1 : 5-diaminoanthraquinone, m. p. 309—310°, not 319° as given by Noelting and Wortmann (A., 1906, i, 291). Conversion of this into anthrarufin proved its constitution. In a similar manner, the constitution of 1 : 8-*dinitro-2-methylanthraquinone*, m. p. 293—295°, was established. It forms white to pale yellow needles, sparingly soluble in organic solvents, but more soluble than the 1 : 5-isomeride. Attempts to obtain higher nitrated derivatives of β-methylanthraquinone were unsuccessful. (Cf. Schaarschmidt and Stahlschmidt, A., 1913, i, 95.) E. H. R.

Neorobin. P. Masucci and G. A. Slothower (*J. Amer. Pharm. Assoc.*, 1923, **12**, 335—338).—"Neorobin," which is prepared by reduction of chrysarobin with tin and acetic acid, is neither a compound of tin nor an acetate. It is at least 50% more active as a reducing agent than chrysarobin, and can be determined by addition of ammoniacal silver nitrate to its solution in acetone, followed by determination of the reduced silver in the usual way.

Chemical Abstracts.

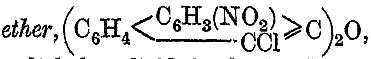
1 : 2 : 8-Trimethoxy-6-methylanthraquinone and 1 : 2 : 8-Trimethoxy-7-methylanthraquinone. J. L. Simonsen (*J. Chem. Soc.*, 1924, **125**, 721—726; cf. *ibid.*, 1921, **119**, 1339).—The condensation of hemipinic anhydride with *m*-cresol using aluminium chloride and boric acid as condensing agents yields mainly 2′-*hydroxy*-3 : 4-*dimethoxy*-4′-*methyl*-2-*benzoylbenzoic acid*, glistening needles, m. p. 229—230°, which on methylation with methyl sulphate gives 2′ : 3 : 4-*trimethoxy*-4′-*methyl*-2-*benzoylbenzoic acid*, glistening prisms, m. p. 198—199°, a small quantity of a *phthalein*, $C_{24}H_{22}O_6$, m. p. 285—287°, being obtained as a by-product in the condensation. Concentrated sulphuric acid at 150° converts the 2′-hydroxy-3 : 4-dimethoxy-4′-methyl-2-benzoylbenzoic acid into the corresponding anthraquinone, but in poor yield, and from the crude hydroxyanthraquinone 1 : 2 : 8-*trimethoxy*-6-*methylanthraquinone*, fine yellow needles, m. p. 164—165°, was obtained by methylation. With *o*-cresol the condensation gave mainly 2′-hydroxy-3 : 4-dimethoxy-3′-methyl-2-benzoylbenzoic acid, bevelled prisms, m. p. 250—251°, accompanied by considerable quantities of a *phthalein*, $C_{24}H_{22}O_6$, m. p. 237—238°, when a large excess of *o*-cresol was used. Methylation converted the benzoylbenzoic acid derivative into 2′ : 3 : 4-*trimethoxy*-3′-*methyl*-2-*benzoylbenzoic acid*, hexagonal prisms, m. p. 199° (*methyl* ester, prisms, m. p. 153—155°), whilst heating with sulphuric acid gave an almost quantitative yield of the crude hydroxyanthraquinone, which was methylated with difficulty to 1 : 2 : 8-*trimethoxy*-7-*methylanthraquinone*, yellow needles, m. p. 209—210°. R. B.

Phenanthrene Series. XXXV. Transformations of Chlorophenanthrenes. J. Schmidt and E. Äckerle (*Ber.*, 1924, **57**, [*B*], 363—369).—An extension of the work of Schmidt and Spoun (A., 1922, i, 665). The preparation of 9 : 9- and 10 : 10-dichloro-2-nitrophenanthrones from 2-nitrophenanthraquinone and phosphorus pentachloride in the presence of benzene is described in detail (the position of the chlorine atoms in these compounds is assigned arbitrarily). 9 : 9-Dichloro-2-nitrophenanthrone is reduced by hydroxylamine hydrochloride or phenylhydrazine to 9-*chloro*-2-*nitro*-10-*hydroxyphenanthrene*, yellow needles, m. p. 223° (*acetate*, m. p. 228°; *benzoate*, m. p. 220°). 10 : 10-Dichloro-2-nitrophenanthrone is converted similarly by hydroxylamine hydrochloride into 10-*chloro*-2-*nitro*-9-*hydroxyphenanthrene*, small, yellow crystals, m. p. 193°. It appears therefore that the halogen atoms of the chloro-2-nitrophenanthrones are retained with unexpected firmness; this view is confirmed by the observation that the α-compound is stable towards molecular silver in the presence of boiling benzene.

4-Nitrophenanthraquinone is converted by phosphorus pentachloride in the presence of benzene into a mixture of 9 : 9-*dichloro*-4-*nitrophenanthrone* (α-compound), pale yellow crystals, m. p. 203°, and 10 : 10-*dichloro*-4-*nitrophenanthrone* (β-compound), m. p. 137°. The former substance is transformed by hydroxylamine hydrochloride or phenylhydrazine into 9-*chloro*-4-*nitro*-10-*hydroxyphenanthrene*, m. p. 203° (*acetate*, pale yellow powder, m. p. 223°; *benzoate*, small, colourless crystals, m. p. 196°). 10-*Chloro*-4-*nitro*-9-*hydroxyphenanthrene* has m. p. 153—154° (*benzoate*, m. p. 188—189°).

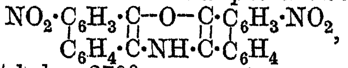
4-Nitrophenanthraquinone is converted by phosphorus pentachloride under pressure at 120° into 9 : 9 : 10 : 10-*tetrachloro-4-nitrodihydrophenanthrene*, slender, brownish-yellow needles, m. p. 164—165°, which is transformed by phenylhydrazine or molecular silver into 9 : 10-*dichloro-4-nitrophenanthrene*, m. p. 136—137°; the chlorine atoms are retained with extraordinary firmness in these compounds, particularly in the latter.

Di-9-chloro-2-nitro-10-phenanthryl ether,



$\left(C_6H_4{<}\begin{matrix}C_6H_3(NO_2)\\ \text{———}CCl\end{matrix}{>}C\right)_2O$,

a brown substance which does not melt below 370°, is obtained as a by-product of the action of acetic anhydride on 9-chloro-2-nitro-10-hydroxyphenanthrene. The latter substance is converted by alcoholic ammonia at 160° into 2-*nitrophenanthroxazine*,



$$\begin{matrix}NO_2\cdot C_6H_3\cdot C\text{—}O\text{—}C\cdot C_6H_3\cdot NO_2\\ C_6H_4\cdot C\cdot NH\cdot C\cdot C_6H_4\end{matrix},$$

which does not melt below 370°. H. W.

Enolisation of Camphor. M. Bredt-Savelsberg, C. A. Heinemann, P. Catharinus, and H. Eibel (*J. pr. Chem.*, 1924, [ii], **107**, 65—86).—The method of Tschugaev and Zerevitinov (A., 1907, ii, 509) for the determination of hydroxyl groups has been applied to a study of the enolisation of camphor. When camphor, which in ether, benzene, or alcohol solution is known to possess the ketonic structure, is brought into contact with a Grignard reagent, enolisation takes place and its extent is determined from the hydrocarbon produced corresponding with the alkyl or aryl group in the Grignard reagent used. Thus magnesium methyl halides give methane, magnesium phenyl bromide gives benzene. The extent of the enolisation depends on a number of factors. (1) The alkyl or aryl group in the Grignard reagent. Equimolecular quantities of camphor and Grignard reagent in ether solution show 29% enolisation with magnesium methyl iodide, 14% with magnesium ethyl iodide, and 25% with magnesium α-naphthyl bromide. In the second case, ethylene is produced as well as ethane, in the ratio of about 3 : 10 at 30°. In amyl ether solution, magnesium phenyl bromide shows 21% enolisation (in ethyl ether solution it was very difficult to determine the benzene formed). (2) The halogen present in the Grignard reagent. With the magnesium methyl halides the enolisation of the camphor increases with the electronegative character of the halogen, from about 14·8% in the case of the iodide to 28·2% with the chloride. (3) The proportions of Grignard reagent and camphor. Excess of Grignard reagent favours enolisation of the camphor. With the proportions ½, 1, 2, and 3 mols. of camphor to 1 mol. of Grignard reagent the enolisation figures were 32·6, 14·9, 16·3, and 16·9%, respectively. (4) The time of reaction. Equilibrium is only reached after a prolonged period. With magnesium methyl iodide, periods of ½, 5, 10, 25, and 40 hours showed enolisation of 13·0, 14·1, 14·9, 30·4, and 44·7%, respectively. (5) The character of the solvent. In amyl ether solution, magnesium methyl iodide enolises camphor to the extent of about 3·6%, against 44·7% in ethyl ether. In a solvent free from oxygen (benzene) the enolisation is 32·5%. (6) The temperature of reaction. With magnesium methyl iodide the enolisation figures in 10 hours were found to be 6·85% at 0° and 14·9% at 20°. The enolisation of camphor by Grignard reagents explains the low yields of tertiary borneols which have been obtained by the Grignard method, as only the keto-form yields a complex from which tertiary borneols are formed. R. B.

Pyroelectricity of Two Derivatives of Camphor. M. R. LUCAS.—(See ii, 224.)

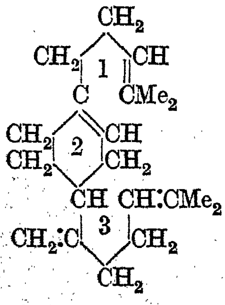
Oxidation of *allo*-Ocimene, Ocimene, and Myrcene. C. J. ENKLAAR (*Chem. Weekblad*, 1924, **21**, 101—102; cf. A., 1906, i, 377).—A sample of *allo*-ocimene (b. p. 98—102°/32 mm.) on treatment with permanganate in dry acetone at 0° was only partly oxidised. The only oxidation product obtained was a neutral substance, allo-*ocimene oxide*, probably $C_{10}H_{16}O$, b. p. 105°/13 mm., d^{20} 0·909, which is neither aldehyde, ketone, nor glycol. By the action of permanganate on ocimene in acetone solution at 56°, an acid (lead salt, crystallising in rhombs) was obtained; this lead salt is suitable for the identification of the terpene. Myrcene under these conditions yields an acid of which the lead salt crystallises in fine needles, readily distinguishable from the ocimene lead salt. By exhaustive treatment of ocimene with permanganate, a mixture was obtained in which only oxalic acid could be identified. S. I. L.

Catalytic Action. IV. A Function of Reduced Copper. S. KOMATSU (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 85—91).—When menthol is passed over reduced copper at 320°, besides the expected menthone, some menthene is formed. The copper therefore acts, like thoria, as a dehydrating agent. In the same way, ethyl alcohol yields acetaldehyde and ethylene, and *iso*propyl alcohol (at 300°) gives acetone and propylene. *cyclo*Hexanol is likewise dehydrogenated and dehydrated; *cyclo*hexene, *cyclo*hexanone, di*cyclo*hexyl ether, and water are produced in quantities agreeing with the author's explanation of the reaction, based on the supposition that dehydration takes place in three directions simultaneously.
W. A. S.

Higher Terpene Compounds. XX. Sesquiterpenes and Sesquiterpene Alcohols of Camphor Oil. L. RUZICKA and M. STOLL (*Helv. Chim. Acta*, 1924, **7**, 260—270).—So-called heavy camphor oil, b. p. 110—140°/12 mm., contains, besides cadinene and bisabolene, a monocyclic *hydrocarbon*, $C_{15}H_{24}$, which was not more exactly characterised, but forms a very stable *dihydrochloride*, an oil, b. p. 125°/0·3 mm., and a bicyclic *hydrocarbon*, $C_{15}H_{24}$, a colourless oil, b. p. 128—135°/12 mm., which must be of the cadinene type since, when dehydrogenated by boiling with sulphur, it gives cadaline. The sesquiterpene alcohol fraction of camphor oil, b. p. 150—160°/12 mm., gives cadaline when dehydrogenated with sulphur. Purification of this alcohol fraction through the benzoate gives 15% of an alcohol, b. p. 155—160°/12 mm., which agrees in properties with Semmler and Rosenberg's sesquicamphenol (A., 1913, i, 378). When this purified alcohol was dehydrogenated with sulphur and the product fractionated, the fraction of b. p. 140—145°/12 mm. contained eudaline whilst that of b. p. 150—165°/12 mm. contained cadaline. Camphor oil therefore contains compounds of both cadinene and eudesmol types, and is unique in this respect. The alcohol fraction was separated by means of phthalic anhydride into primary, secondary, and tertiary constituents. The *primary* sesquicamphenol has b. p. 156—158°/12 mm., $[\alpha]_D$ +2·2°, d_4^{18} 0·9568, n_D^{18} 1·5045. It is reduced by hydrogen in presence of platinum black to a *dihydrosesquicamphenol*, $C_{15}H_{28}O$, a colourless, viscous oil, b. p. 152—153°/12 mm., d_4^{22} 0·9150, n_D^{22} 1·4755. From the purified sesquiterpene alcohols a *secondary* sesquicamphenol, b. p. 160—162°/12 mm., $[\alpha]_D$ −5·2°, d_4^{20} 0·9720, n_D^{20} 1·5066, was obtained, which by catalytic reduction gave a dihydrosesquicamphenol, b. p. 150—152°/12 mm., d_4^{15} 0·9510, n_D^{15} 1·4892; whilst from a crude fraction of alcohols, b. p. 140—170°/12 mm., the secondary alcohol appeared to be a mixture of $C_{15}H_{26}O$ and $C_{15}H_{24}O$. One of these alcohols is of the cadinene type. The tertiary alcohol fraction, obtained from the sesquiterpene alcohols purified through the benzoate, had b. p. 156°/12 mm., d_4^{20} 0·9665, n_D^{20} 1·5050, and by dehydrogenation gave both eudaline and cadaline. Two tertiary sesquiterpene alcohols are therefore present in camphor oil.

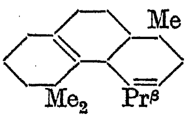
E. H. R.

Higher Terpene Compounds. XXI. Constitution and Isomerisation of α-Camphorene. L. Ruzicka and M. Stoll (*Helv. Chim. Acta*, 1924, 7, 271—282).—α-Camphorene, the diterpene found by Semmler and Rosenberg in camphor oil (A., 1913, i, 378), is known to be a monocyclic compound related to myrcene, but its constitution has not been determined. Myrcene is probably a mixture of isomerides, $CMe_2{:}CH{\cdot}[CH_2]_2{\cdot}C({:}CH_2){\cdot}CH{:}CH_2$ (I) and $CH_2{:}CMe{\cdot}[CH_2]_3{\cdot}C({:}CH_2){\cdot}CH{:}CH_2$ (II), but experiments on its decomposition by ozone indicate that (I) predominates, since only succinic acid was obtained and no trace of glutaric acid. Assuming that myrcene polymerises to α-camphorene by a process similar to the polymerisation of isoprene to dipentene, the annexed formula is obtained for α-camphorene. This formula harmonises with the physical constants of α-camphorene, and with its isomerisation products. When boiled with 95% formic acid, α-camphorene is converted into a *bicyclic diterpene*, a viscous oil, b. p. 192—194°/12 mm., d_4^{14} 0·9086, n_D^{14} 1·5104. The side chain 1 of the above formula has the configuration of a geranyl derivative, and ring closure is to be expected. More prolonged heating of α-camphorene or of the bicyclic compound with formic acid results in the formation of a *tricyclic diterpene*, b. p. 180—181°/12 mm., d_4^{14} 0·9475, n_D^{14} 1·5201. In the above formula, the ring 2 and the first three carbon atoms of side chain 3 have the dipentene structure, and a wandering of the

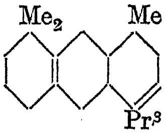


double bond into the ring may take place, analogous to the isomerisation of dipentene to α- and γ-terpenes. This would give configurations leading, after ring closure, to the formation of either a phenanthrene or an anthracene derivative,

(III.)



or



(IV.)

By oxidation with manganese dioxide and sulphuric acid the tricyclic α-camphorene gave, besides mellophanic acid, which might result from either formula, pyromellitic acid, which can, as far as is known, only result from the anthracene structure. It is probable, therefore, that the tricyclic compound has structure IV, for which the name isotricyclo*camphorene* is proposed, III being designated tricyclo*camphorene*. By catalytic hydrogenation, only two atoms of hydrogen were taken up, *dihydro*(?iso)tricyclo*camphorene* being formed, a colourless, viscous oil, b. p. 176°/12 mm., d_4^{14} 0·9410, n_D^{14} 1·5118. Oxidation of octahydro-α-camphorene with manganese dioxide and sulphuric acid gave, besides mellophanic acid and pyromellitic acid, terephthalic acid, which is additional evidence in support of the suggested α-camphorene formula. To the two known types of the diterpene series, the abietic acid and dextropimaric acid types, must now be added the camphorene type; in all of these the carbon skeleton is composed of four associated isoprene residues. (Cf. A., 1923, i, 818—819.) E. H. R.

Classification of the Resinic Acids from Conifers. O. Aschan (*Chem.-Ztg.*, 1924, **48**, 149—150).—The acids occurring in pine resins together with some of their derivatives may be divided into three classes, viz., the natural acids such as pimaric and sapic acids; the colophony acids (*iso*pimaric and abietic acids) which are formed by heating the natural sapic acids; and the sylvic acids formed by treating other resinic acids with mineral acids. Of the acids of the first group, the pimaric acids are stable in the air and difficultly soluble in organic solvents, have high melting points, and absorb two atoms of hydrogen in the presence of platinum black; the sapic acids, on the other hand, are very unstable, have low melting points, and dissolve readily in organic solvents. The *iso*pimaric acids are unstable in air, absorb two or four atoms of hydrogen, are fairly easily soluble in hot organic solvents, and melt between 150° and 160°, whilst the abietic acids absorb only two atoms of hydrogen, are difficultly soluble in organic solvents, and melt at about 200°. The true sylvic acids formed by treating the natural acids with hydrochloric or sulphuric acid are stable in the air, absorb four atoms of hydrogen or four hydroxyl groups when treated with permanganate, are difficultly soluble in organic solvents, and have high melting points, whilst the *iso*sylvic acids, formed by splitting off water or hydrogen halide from the corresponding additive products of other resinic acids, are relatively easily soluble in organic solvents and have low melting points. A. R. P.

Synthesis of 7-Ethoxy-4′-dimethylaminoflavone. H. Nägeli and J. Tambor (*Helv. Chim. Acta*, 1924, 7, 333—336).—Condensation of *p*-dimethylaminobenzaldehyde in alcoholic potassium hydroxide solution with resacetophenone monoethyl ether (2-hydroxy-4-ethoxyacetophenone) gives *2-hydroxy-4-ethoxy-4′-dimethylaminochalkone* (*2-hydroxy-4-ethoxyphenyl 4-dimethylaminostyryl ketone*), red needles, m. p. 149°, giving an intense green fluorescence in organic solvents. The *acetyl* derivative forms yellow needles, m. p. 88°. Treatment of the acetyl compound in carbon tetrachloride solution with pyridine dibromide gave a chalkone dibromide which, without further examination, was converted by alcoholic potassium hydroxide into *7-ethoxy-4′-dimethylaminoflavone*, orange needles, m. p. 183°. Its solution in concentrated sulphuric acid is yellow with a weak green fluorescence; in organic solvents the fluorescence is intense.

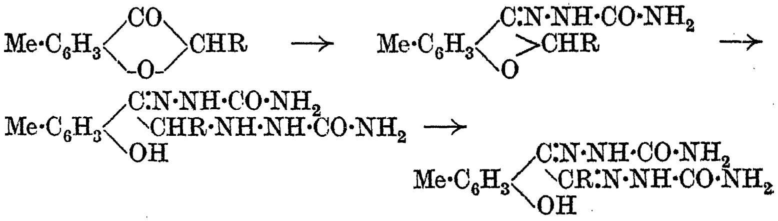
2 : 4-*Diethoxyphenyl 4-dimethylaminostyryl ketone*, from resacetophenone diethyl ether, as above, forms bright yellow needles, m. p. 128°. o-*Hydroxyphenyl* p-*dimethylaminostyryl ketone* forms red needles, m. p. 176°. The corresponding p-*hydroxyphenyl* p-*dimethylaminostyryl ketone* forms orange leaflets, m. p. 205°; *acetyl* derivative, brownish-yellow needles, m. p. 136°; *methyl* ether, yellow leaflets, m. p. 126°; *ethyl* ether, orange leaflets, m. p. 113°. 2 : 3-*Dimethoxyphenyl* p-*dimethylaminostyryl ketone* forms brown needles, m. p. 80°, and o-*anisyl* p-*dimethylaminostyryl ketone*, yellow leaflets, m. p. 101°. E. H. R.

Action of the Oxides and the Oxy-acids of Nitrogen on Diphenylene Oxide. H. Ryan and N. Cullinane (*Sci. Proc. Roy. Dubl. Soc.*, 1924, **17**, 321—326).—Whilst diphenylene oxide is unaffected by mixtures of cold nitric and glacial acetic acids, nitric acid in carbon tetrachloride solution, fuming nitric acid in warm acetic acid solution, nitrous fumes, or nitrogen peroxide in carbon tetrachloride or acetic acid, converts it mainly into 3-nitrodiphenylene oxide (cf. Borsche and Bothe, A., 1908, i, 528). Gaseous nitrogen peroxide gives the 3 : 6-dinitro derivative (Mailhe, A., 1912, i, 548), which also results when the mononitro derivative is nitrated. By still more vigorous nitration, first 1 : 3 : 6(?)-*trinitrodiphenylene oxide* (blunt prisms, m. p. 223°), and then 1 : 3 : 6 : 8(?)-*tetranitrodiphenylene oxide* (colourless plates, m. p. 283°) are produced (cf. Mailhe, *loc. cit.*; Borsche and Scholten, A., 1917, i, 390).
W. A. S.

Valency Requirements of Alkyl [Radicals]. K. von Auwers and G. Wegener (*J. pr. Chem.*, 1923, [ii], **106**, 226—252).—When the silver compound of benzamide is treated with methyl iodide at the ordinary temperature, 52% undergoes change in 11 days, the product affording, with picric acid, ammonium and benzimino methyl ether picrates. When ethyl iodide is used (91% interaction in 5·5 days) the corresponding products are ethyl benzoate, benzonitrile, ammonium picrate, and benzimino ethyl ether dipicrate (?), m. p. 146—147°. When allyl iodide is used, the initial products isolated are benzamide and benzimino *n*-propyl ether (a colourless oil, b. p. 113—116°/12 mm.), the latter with picric acid affording ammonium picrate (cf. Wheeler, A., 1898, i, 185). In none of the above cases were *N*-ethers, described by Wheeler, detected.

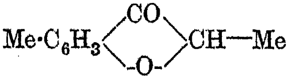
s-Formylphenylhydrazine, when treated with methyl iodide in presence of sodium ethoxide, gives a mixture of products; with allyl bromide as alkylating agent the hydrazine is rapidly and quantitatively converted into *β-formyl-α-allyl-α-phenylhydrazine*, white prisms, m. p. 57—58°, b. p. 183°/13 mm. When benzyl chloride is used, *β-formyl-α-benzyl-α-phenylhydrazine* (white prisms, m. p. 108—109°) is formed.

The authors have studied the scission of 4-methyl-1-alkylcoumaranones, using semicarbazide:

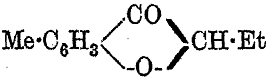


$$\mathrm{Me{\cdot}C_6H_3}\left\langle\begin{array}{l}\mathrm{CO}\\ \mathrm{O}\end{array}\right\rangle\mathrm{CHR} \longrightarrow \mathrm{Me{\cdot}C_6H_3}\left\langle\begin{array}{l}\mathrm{C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2}\\ \mathrm{O}\end{array}\right\rangle\mathrm{CHR} \longrightarrow \mathrm{Me{\cdot}C_6H_3}\left\langle\begin{array}{l}\mathrm{C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2}\\ \mathrm{CHR{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2}\\ \mathrm{OH}\end{array}\right. \longrightarrow \mathrm{Me{\cdot}C_6H_3}\left\langle\begin{array}{l}\mathrm{C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2}\\ \mathrm{CR{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2}\\ \mathrm{OH}\end{array}\right.$$

The coumaranone (1 mol.) was left in aqueous-alcoholic solution at 45—50° in presence of 2·5 mols. of semicarbazide hydrochloride and sodium acetate and the time required for the initial separation of the disemicarbazone noted. The times (hours) required were as follows: R=Me, 4; R=Et, 14; R=Prᵅ, 4; R=PrᵅCH₂·, 6·5; R=*n*-pentyl, 7·5; R=Ph·CH₂, 14·5. These results agree well with those *e.g.* of Meerwein (A., 1920, i, 2), as is evident from the following formulæ:



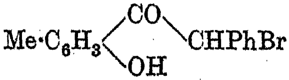
$$\mathrm{Me{\cdot}C_6H_3}\left\langle\begin{array}{l}\mathrm{CO}\\ \mathrm{O}\end{array}\right\rangle\mathrm{CH{-}Me}$$



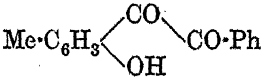
$$\mathrm{Me{\cdot}C_6H_3}\left\langle\begin{array}{l}\mathrm{CO}\\ \mathrm{O}\end{array}\right\rangle\mathrm{CH{\cdot}Et}$$

A phenyl radical (possessing greater valency requirements than an alkyl radical) in position 1 facilitates scission of coumaranones to such an extent that it is impossible to convert (I) into 1-phenyl-

(I.)



$$\mathrm{Me{\cdot}C_6H_3}\left\langle\begin{array}{l}\mathrm{CO{\cdot}CHPhBr}\\ \mathrm{OH}\end{array}\right.$$



$$\mathrm{Me{\cdot}C_6H_3}\left\langle\begin{array}{l}\mathrm{CO{\cdot}CO{\cdot}Ph}\\ \mathrm{OH}\end{array}\right.$$

(II.)

coumaranone satisfactorily, the latter substance being accompanied by (II) and a little *o*-benzoyl-*p*-cresotic acid (produced by the oxidation of 1-phenylcoumaranone). Since coumaranones not alkylated in position 1 cannot be split with semicarbazide, hydrogen must have a lower valency requirement than an alkyl radical. 1 : 1-Dialkylcoumaranones are less readily split by reagents than coumaranone itself, only giving monosemicarbazones with difficulty; this is probably due to steric hindrance. Coumaranones containing the 1-grouping >CR(OR), where R=H or alkyl, are readily split, but this may be attributed to the interaction of the ·OR radical with semicarbazide.

The authors compare and contrast the scission of coumaranones with that of benzoxazoles (Skraup, A., 1919, i, 598) and of phthalides (Teppema, A., 1923, i, 256), from the point of view of valency requirements of the groups present.

A number of new compounds are described: *α-Bromo-*n*-valeryl bromide* is a colourless liquid, b. p. 190°; *α-bromo-*n*-hexanoyl bromide* is a colourless liquid, b. p. 201—210°/ordinary press. (decomp.) or 85—90°/12—13 mm.; *α-bromo-*n*-heptanoyl bromide*, a pale yellow liquid, has b. p. 101—102°/9 mm.; *α-bromopalmityl bromide* is a white solid, charring when heated. These bromides, condensed with *p*-cresol methyl ether (A., 1918, i, 27), give rise to ketones: *3-α-bromo-*n*-valeroyl-*p*-cresol* forms yellow plates, m. p. 51—52°; *3-α-bromo-*n*-hexanoyl-*p*-cresol*, yellow needles, has m. p. 30·5—31·5°; *3-α-bromo-*n*-heptanoyl-*p*-cresol*, yellow needles, has m. p. 49—50°; *3-α-bromopalmitoyl-*p*-cresol* forms yellow crystals, m. p. 46—47°. The ketones, with alcoholic sodium acetate, afford coumaranones: *4-methyl-1-*n*-propylcoumaranone*, a yellow oil, has b. p. 133—134°/11 mm., d_4^{20} 1·064, n_{He}^{20} 1·5445; *4-methyl-1-*n*-butylcoumaranone*, a yellow oil, has b. p. 166—168°/17 mm., and cannot be purified through the semicarbazone, since the disemicarbazone is formed even in the cold; *4-methyl-1-*n*-pentylcoumaranone*, a yellow oil, has b. p. 175°/18 mm.; *4-methyl-1-*n*-tetracaidecylcoumaranone* forms waxy white crystals, m. p. 68—69°, and when heated in alcoholic solution with *p*-nitrophenylhydrazine hydrochloride affords the pp-*dinitro-osazone* of p-*cresyl tetracaidecyl ketone*, $OH\cdot C_6H_3Me\cdot C(:N\cdot NH\cdot C_6H_4\cdot NO_2)\cdot C(:N\cdot NH\cdot C_6H_4\cdot NO_2)\cdot C_{14}H_{29} + 1(\text{or } 2)H_2O$, red crystals, m. p. 164—165° (with previous softening); *4-methyl-1-benzylcoumaranone*, from 2-hydroxy-4-methylcoumarilic ester, sodium ethoxide, and benzyl chloride, forms white prisms or needles, m. p. 50—51°, b. p. 200—210°/13—14 mm. The benzyl compound is accompanied by *2-benzoxy-4-methylcoumarilic acid*, white needles, m. p. 146—147°, and is converted by *p*-nitrophenylhydrazine hydrochloride into the pp-*dinitro-osazone* of p-*cresyl benzyl diketone*, decomp. 223° (if heated rapidly). *4-Methyl-1:1-dibenzylcoumaranone* forms colourless needles or rhombohedra, m. p. 122—123°.

The following were obtained by treating coumaranones with semicarbazide: *disemicarbazone* of p-*cresyl* n-*propyl diketone*, decomp. 212—213° (rapid heating); *disemicarbazone* of p-*cresyl* n-*butyl diketone*, m. p. or decomp. 213—214° (rapid heating); *disemicarbazone* of p-*cresyl* n-*pentyl diketone*, m. p. 208—216°; *disemicarbazone* of p-*cresyl benzyl diketone*, m. p. 222° (rapid heating).

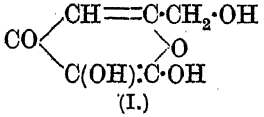
E. E. T.

Hydroxyhydrindone and Chromanone. F. Mayer and L. van Zütphen (*Ber.*, 1924, 57, [*B*], 618).—The product, m. p. 111°, obtained by the action of aluminium chloride on *o*-β-chloropropionylphenol and considered to be 4-ketochroman (Mayer and van Zütphen, this vol., i, 410) is shown to be 7-hydroxy-α-hydrindone (Knake and Salkowski, A., 1916, i, 820; von Auwers and Hilliger, A., 1917, i, 38).

H. W.

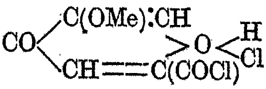
Synthesis of 7-Methoxychromanone. A. E. TSCHITSCHIBABIN (*Ber.*, 1924, **57**, [*B*], 617).—The synthesis of 7-methoxychromanone by Pfeiffer and Oberlin (cf. this vol., i, 413) from resorcinol monomethyl ether and iodopropionic acid had already been effected by Tschitschibabin and Nikitin in 1911 (A., 1911, i, 1007). F. A. M.

The Constitution of Kojic Acid, a γ-Pyrone Derivative formed by *Aspergillus oryzæ* from Carbohydrates. T. YABUTA (*J. Chem. Soc.*, 1924, **125**, 575—587).—Previous work (A., 1922, i, 939) has shown that kojic acid (I) is probably the alcohol corresponding with comenic acid. Interconversion by oxidation of kojic acid or reduction of comenic acid has not been accomplished, but both compounds furnish the same 4 : 5-dihydroxy-2-methylpyridine. Kojic acid on treatment with thionyl chloride yields 5-*hydroxy*-2-*chloromethyl*-γ-*pyrone*, needles, m. p. 166—167°. The latter gives the corresponding 5-*benzoyloxy* derivative, prisms, m. p. 117—118°, and the 5-*methoxy* derivative, needles, m. p. 119—121°, and on reduction with zinc dust and acetic acid gives allo*maltol* (5-hydroxy-2-methyl-γ-pyrone), prisms, m. p. 166°. *Allo*maltol is distinct from maltol (Brand, A., 1894, i, 270) and from *iso*maltol (Backe, A., 1910, i, 225, 544), the distinction being confirmed by the preparation of the following derivatives. Allo*maltol methyl* ether (5-methoxy-2-methyl-γ-pyrone), prisms, m. p. 70—71°, b. p. (approx.) 93°/0·1 mm.; *benzoyl*allo*maltol* (3-benzoyloxy-6-methyl-γ-pyrone), prisms, m. p. 128—129°; *phenylcarbamate* of allo*maltol*, $NHPh\cdot CO\cdot C_6H_5O_3$, plates, m. p. 186—188°; *bromo*allo*maltol* (6-bromo-5-hydroxy-2-methyl-γ-pyrone), crystals, m. p. 171—173°. *Benzeneazo*allo*maltol* (6-benzeneazo-5-hydroxy-2-methyl-γ-pyrone), by treating *allo*maltol in solution with diazobenzene acetate, forms reddish-brown needles, no definite m. p.


(I.)

Oxidation of the following kojic acid derivatives did not give the corresponding comenic acid derivatives: monobenzoyl kojic acid; *monoethyl ether* of *kojic acid* (5-ethoxy-2-hydroxymethyl-γ-pyrone), prepared by the interaction of kojic acid, ethyl *p*-toluenesulphonate, and sodium ethoxide in alcohol, needles, m. p. 110°; 5-*ethoxy*-2-*hydroxymethyl*-4-*pyridine*, prepared from kojic acid monoethyl ether, and isolated as the *picrate*, needles, m. p. 184—185°; 5-hydroxy-2-chloromethyl-γ-pyrone and its methyl ether; 5-*hydroxy*-2-*iodomethyl*-γ-*pyrone*, prepared from the corresponding chloro-compound as crystalline plates; 5-*methoxy*-2-*iodomethyl*-γ-*pyrone*, prisms, m. p. 135—137°.

The following derivatives of comenic acid were prepared, but reduction did not give the corresponding kojic acid derivatives. *Benzoylcomenic acid*, prisms from alcohol, m. p. 227—228°; *methyl ether* of *comenic acid*, prisms, m. p. 280—282°; *methyl ether* of *methyl comenate*, m. p. 197°; *methyl ether* of *ethyl comenate*, m. p. 156°; the *hydrochloride* of the *methyl ether* of *comenyl chloride* (II), prepared by the


(II.)

action of thionyl chloride on comenic acid methyl ether, prisms, m. p. 103°; the *methyl ether* of *comenyl chloride*, prepared from the previous compound by the action of sodium acetate, m. p. 148°; *comenamide methyl ether*, prepared by the action of ammonia on (II), needles, m. p. 178°. The catalytic reduction of the methyl ether of comenyl chloride by Rosenmund's method (A., 1918, i, 300; 1921, ii, 320, 392) failed owing to the instability of the pyrone nucleus. *Comenamic acid methyl ether* (5-methoxy-4-pyridone-2-carboxylic acid) was prepared by the action of ammonia on comenic acid methyl ether; *ammonium* salt, needles, m. p. 269°; *hydrochloride*, prisms. Thionyl chloride introduces chlorine into the 4-position of the methyl ether, giving 4-*chloro*-5-*methoxypyridine*-2-*carboxylic acid chloride*, which Rosenmund's method also failed to reduce. The acid chloride was converted into 4-*chloro*-5-*methoxypyridine*-2-*carboxylic acid*, prisms, m. p. 209°, into the *amide*, needles, m. p. 207—208°, into the *methyl* ester, prisms, m. p. 167°, and into the *ethyl* ester, prisms, m. p. 140°.

*allo*Maltol methyl ether, prepared either by the methylation of *allo*maltol or by the reduction of 5-methoxy-2-chloromethyl-4-pyrone, when heated with ammonia in a closed tube at 100° gives 5-*methoxy*-2-*methyl*-4-*pyridone*, needles, m. p. 115°, which gives a *picrate*, needles, m. p. 205—206°. The dimethyl ether of kojic acid, when similarly treated, yields the corresponding pyridine derivative, which distils at 200°/1 mm., and on heating with red phosphorus and hydriodic acid gives 4 : 5-*dihydroxy*-2-*methyl pyridine*, prisms, decomp. 280°, and crystallising $+1H_2O$ at low temperatures.

Comenic acid when heated with ammonia under pressure gives comenamic acid, which when treated with phosphorus pentachloride and then reduced with tin and hydrochloric acid gives the same 4 : 5-dihydroxy-2-methylpyridine. The dihydroxypicolines obtained thus from both acids gave on methylation the same 5-*methoxy*-1 : 2-*dimethyl*-4-*pyridone* ($+3H_2O$), colourless needles, m. p. 98°. This compound is also formed by treating *allo*-maltol methyl ether with methylamine, thus confirming the position of the methyl groups. Comenamic acid on methylation gives similarly 5-*methoxy*-1-*methyl*-4-*pyridone*-2-*carboxylic acid* ($+4H_2O$), needles, m. p. 208°. F. G. M.

Action of Sodium Sulphite on Coumarins. B. B. DEY and K. K. ROW (*J. Chem. Soc.*, 1923, **125**, 554—564).—Coumarins and many substituted coumarins react readily with sodium hydrogen sulphite to give β-sulphonic acids, *e.g.*,

$$OH\cdot C_6H_4\cdot CH(SO_3Na)\cdot CH_2\cdot CO_2H,xH_2O.$$

These yield halogen and nitro derivatives, which when heated with sulphuric acid give sulphur dioxide and the corresponding *Bz*-substituted coumarins, and when heated with potassium hydroxide solution give the corresponding potassium coumarates. The ethers of coumarinic acid when boiled with sodium hydrogen sulphite solution and then with sodium hydroxide solution give the corresponding ethers of coumaric acid.

Thus coumarin when boiled with aqueous sodium hydrogen sulphite gives *sodium dihydrocoumaric acid* β-*sulphonate*, colourless plates from water, decomp. 175—176° (*potassium*, *barium*, and *calcium* salts described). 6-Nitrocoumarin gives *sodium* 5-*nitrodihydrocoumaric acid* β-*sulphonate*, whilst 3-chloro- and 3-bromo-coumarin both give benzfuran-2-carboxylic acid (cf. Fittig, A., 1883, 474). 3 : 6-Dinitrocoumarin gives 5-nitrosalicylaldehyde, whilst *o*-coumaric acid behaves like coumarin itself. 3-Acetylcoumarin gives *sodium* α-*acetyldihydrocoumaric acid* β-*sulphonate*, white crystals, m. p. 163° (decomp.). Sodium dihydrocoumaric acid β-sulphonate when treated in aqueous solution with chlorine gives *sodium* 3 : 5-*dichlorodihydrocoumaric acid* β-*sulphonate* (colourless needles), which on heating alone or with sulphuric acid gives sulphur dioxide and 6 : 8-*dichlorocoumarin*, crystalline nodules, m. p. 160°, subliming at 130—135° in colourless needles. Bromine similarly gives *sodium* 3 : 5-*dibromodihydrocoumaric acid* β-*sulphonate* (plates), which on heating gives 6 : 8-*dibromocoumarin*, needles, m. p. 176°. Iodine gives *sodium* 5-*iododihydrocoumaric acid* β-*sulphonate*, colourless plates, which on heating yields 6-*iodocoumarin*, needles, m. p. 165°.

Sodium 5-nitrodihydrocoumaric acid β-sulphonate on bromination gives *sodium* 3-*bromo*-5-*nitrodihydrocoumaric acid* β-*sulphonate*, colourless plates, decomp. 210°, on iodination *sodium* 3-*iodo*-5-*nitrodihydrocoumaric acid* β-*sulphonate*, and on treatment with fuming nitric acid gives *sodium* 3 : 5-*dinitrodihydrocoumaric acid* β-*sulphonate*.

8-*Bromo*-6-*nitrocoumarin*, colourless needles from acetic acid, m. p. 200°, is obtained by heating the corresponding sodium dihydrocoumaric acid β-sulphonate with sulphuric acid, and on reduction with 5% acetic acid and iron filings gives 8-*bromo*-6-*aminocoumarin*, yellow needles, m. p. 200°. The latter gives an *acetyl* derivative, colourless needles, m. p. 249°, a *benzoyl* derivative, needles from acetic acid, m. p. 217°, a *hydrochloride*, colourless prisms, darkening at 235°, m. p. 246° (decomp.), and a *picrate*, yellow needles, m. p. 180—181° (decomp.). 8-*Iodo*-6-*nitrocoumarin*, similarly prepared, colourless needles, m. p. 249° (decomp.), on reduction gives 8-*iodo*-6-*aminocoumarin*, orange-yellow needles, m. p. 210°, which yields an *acetyl* derivative, needles, m. p. 275° (decomp.). 6 : 8-*Dinitrocoumarin*, similarly prepared, forms yellow needles, m. p. 158°.

The following *o*-coumaric acids were prepared by treating the corresponding sodium dihydrocoumaric acid β-sulphonates with boiling 20% potassium hydroxide solution and then acidifying. The acids on fusion with potassium hydroxide lose carbon dioxide, giving styrene derivatives. 5-*Chlorocoumaric acid*, needles, m. p. 228° (decomp.); 5-*bromocoumaric acid*, needles, m. p. 224° (decomp.); 3 : 5-*dichlorocoumaric acid*, crystals, m. p. 242° (decomp.), *methyl* ester, colourless needles, m. p. 176°; 3 : 5-*dibromocoumaric acid*, needles, m. p. 238° (decomp.), *methyl* ester, needles, m. p. 173°, *ethyl* ester, spear-shaped crystals, m. p. 128°, *acetyl* derivative, needles, m. p. 201°. 5-*Nitrocoumaric acid*, colourless needles,

m. p. 247° (decomp.), *silver* salt, insoluble and orange-coloured, *methyl* ester, colourless needles, m. p. 211°, *acetyl* derivative, needles, m. p. 217°, immediately resolidifying, and melting again at 259°. 3-*Bromo*-5-*nitrocoumaric acid*, colourless needles, m. p. 234° (decomp.), *methyl* ester, needles, m. p. 212°, *ethyl* ester, fern-shaped crystals, m. p. 184°, *acetyl* derivative, needles, m. p. 186° (decomp.). 5-*Nitro*-4-*methylcoumaric acid*, colourless needles, m. p. 219° (decomp.), *silver* salt, deep orange-red, *methyl* ester, needles, m. p. 187°, *ethyl* ester, needles, m. p. 160°; the acid itself, on fusion with potassium hydroxide, gives 5-nitro-2-methoxy-4-methylcinnamic acid, *methyl* ester, needles, m. p. 136°.

The methyl ethers of coumarinic and 5-nitrocoumarinic acids when boiled with 20% sodium sulphite solution were smoothly converted into the ethers of the corresponding coumaric acids.

α-*Naphthacoumaric acid*, prepared from α-naphthapyrone, needles, m. p. 167° (decomp.), *silver* salt, pale yellow. 4-*Nitro*-α-*naphthacoumaric acid*, prepared from 6-nitronaphthapyrone, small crystals, m. p. 179—180° (decomp.), *silver* salt, orange.

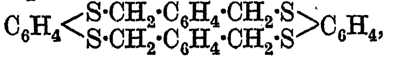
An aqueous solution of α-1 : 8-*iso*naphthoxazone when boiled with sodium sulphite and then with potassium hydroxide, and finally neutralised, gave 6-*hydroxyquinoline*-5-β-*acrylic acid*, $OH \cdot C_9H_5N \cdot CH\colon CH \cdot CO_2H$, white powder, m. p. 220° (decomp.); *silver* salt, pale yellow. The acid, when heated with sulphuric acid, gave the original *iso*naphthoxazone. F. G. M.

Fluorescence. J. TRÖGER and O. GRÜNTHAL (*J. pr. Chem.*, 1923, [ii], **106**, 173—202; cf. A., 1923, i, 355).—The authors have prepared a number of arylsulphonearylideneacetonitriles of the type $R \cdot CH\colon C(SO_2R')CN$ (cf. A., 1908, i, 798), and recorded the fluorescence (if any) of their solutions in concentrated sulphuric acid, glacial acetic acid, etc. R=2-hydroxy-1-naphthyl, R′=Ph, lemon-yellow prisms, m. p. 221° (decomp.): this *nitrile* gives an intense green fluorescence in cold glacial acetic acid; the green fluorescence observed in concentrated sulphuric acid becomes blue on standing, probably owing to the formation of 2-benzenesulphonyl-4 : 3-β-naphthapyrone, which results when the yellow compound is heated with acetic anhydride. R=2-hydroxy-1-naphthyl, R′=*p*-tolyl: this *nitrile* [lemon-yellow prisms, m. p. 232° (decomp.)] exhibits fluorescence similar to the last compound and with acetic anhydride affords 2-*p*-toluenesulphone-*p*-naphthapyrone. R=2-hydroxy-1-naphthyl, R′=*p*-chlorophenyl: this *nitrile* [lemon-yellow prisms, m. p. 254° (decomp.)] shows fluorescence as above, and with acetic anhydride gives 2-*p*-chlorobenzenesulphonyl-β-naphthapyrone. R=2-hydroxy-1-naphthyl, R′=*o*-anisyl: this *nitrile* [sulphur-yellow prisms, m. p. 241° (decomp.)] exhibits fluorescence as above and is converted by acetic anhydride into 2-*o*-*anisylsulphone*-β-*naphthapyrone*, reddish-yellow prisms, m. p. 280° (decomp.). R=2-hydroxy-1-naphthyl, R′=β-naphthyl: this *nitrile* [yellow prisms, m. p. 198° (decomp.)] exhibits fluorescence as above and with acetic anhydride affords 2-β-*naphthalenesulphonylnaphthapyrone*, yellow prisms, m. p. 234° (decomp.). R=2-methoxy-

1-naphthyl, R′=Ph: this *nitrile* (prisms, m. p. 188°) shows the above type of fluorescence. R=2-methoxy-1-naphthyl, R′=*p*-tolyl: this *nitrile* (yellow prisms, m. p. 197°) develops fluorescence slowly in the above solvents, as is the case with the *nitrile* (sulphur-yellow prisms, m. p. 206°) having R=2-methoxy-1-naphthyl and R′=*p*-chlorophenyl. R=2 : 7-dihydroxynaphthyl, R′=*p*-tolyl: this *nitrile* [yellowish-green prisms, m. p. 288° (decomp.)] shows no fluorescence in sulphuric acid solution, owing to the fact that 9-acetoxy-2-*p*-toluenesulphonyl-β-naphthapyrone (m. p. 251°), which results when it is heated with acetic anhydride, is non-fluorescent under similar conditions. The *nitrile* having R=2 : 7-dihydroxynaphthyl and R=Ph forms brownish-green prisms, m. p. 246° (decomp.), and behaves similarly to the tolyl derivative. Other *nitriles* giving non-fluorescent solutions in sulphuric acid are those in which R=*o*-hydroxyphenyl, R′=Ph (white crystals, m. p. 160°), and R=*m*-acetoxyphenyl, R′=*p*-tolyl (grey leaflets, m. p. 134°). The *nitrile* containing R=2 : 5-dihydroxyphenyl, R′=*p*-tolyl [yellow needles, m. p. 224° (decomp.)], develops very little fluorescence and on boiling in alcoholic solution passes into 3-*p*-toluenesulphonyl-6-hydroxycoumarin, the latter substance possessing very slight fluorescent properties. The *nitriles* (canary-yellow prisms, m. p. 159° and 150°, respectively) containing R=2 : 5-dimethoxyphenyl, R′=Ph, and R=2 : 5-dimethoxyphenyl, R′=*p*-tolyl, develop fluorescent effects slowly in acid solution. The *nitriles* containing R=3 : 4-dihydroxyphenyl, R′=*p*-tolyl [yellow prisms, m. p. 183° (decomp.)], and R=3 : 4-methylenedioxy, R′=*p*-tolyl (pale yellow leaflets, m. p. 168°) exhibit no fluorescent effects. On the other hand, when R=2 : 4-dihydroxyphenyl, R′=Ph (yellow prisms, m. p. 237°), marked fluorescence is shown by the *nitrile* in sulphuric acid solution. Moderate fluorescent effects are observed with the *nitrile* having R=2 : 4-dihydroxyphenyl, R′=*p*-tolyl [yellow prisms, m. p. 247° (decomp.)], this nitrile being converted by acetic anhydride into 3-*p*-toluenesulphonyl-7-acetoxycoumarin. Similar properties apply to the *nitrile* in which R=2 : 4-dihydroxyphenyl, R′=*p*-chlorophenyl [sulphur-yellow prisms, m. p. 232° (decomp.)], this compound passing, in boiling alcoholic solution, into 3-*p*-chlorobenzenesulphonyl-7-hydroxycoumarin (m. p. 232°). A sulphuric acid solution of the *nitrile* having R=2 : 4-dihydroxyphenyl, R′=*o*-anisyl (yellow prisms, m. p. 198°) slowly develops fluorescence. The following *nitriles* show no fluorescence: (1) R=2 : 4-dihydroxyphenyl, R′=β-naphthyl, sulphur-yellow prisms, m. p. 253° (decomp.), and (2), R=2 : 4-dimethoxyphenyl, R′=Ph, yellow needles, m. p. 154°.

From the above, it is seen that strongly fluorescent solutions (in concentrated sulphuric acid) are obtained from nitriles possessing a hydroxyl group in the ortho-position to the unsaturated side chain. Other theoretical points are discussed, for which the original should be consulted. E. E. T.

Attempted Syntheses of *meta*-Related Ring Systems. II. F. Reindel and L. Schuberth (*Ber.*, 1924, 57, [*B*], 369—371; cf. Reindel and Siegel, A., 1923, i, 916).—The action of *m*-xylylene bromide on pyrocatechol, resorcinol, or quinol in alcoholic solution in the presence of sodium alkoxide yields only mixtures of products which could not be purified satisfactorily. Better results are obtained with the monomethyl ethers, whereby m-*xylenyl di*-o-*anisyl ether*, $C_6H_4(CH_2·O·C_6H_4·OMe)_2$, colourless needles, m. p. 115°, and m-*xylenyl di*-p-*anisyl ether*, quadratic leaflets, m. p. 128°, are isolated; resorcinol methyl ether gives a compound, b. p. 121°/10 mm., which contains halogen. The compounds, however, are not adapted to the production of *meta*-related ring systems, since they cannot be demethylated without extensive decomposition of the molecule. Attempts to replace methyl by more readily eliminable radicals (acetyl, benzoyl, or carbethoxyl) did not lead to the desired result owing to the ready fission of the compounds into their components.

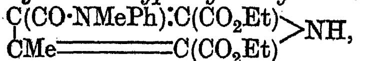
m-Dithiolbenzene is converted by *m*-xylylene bromide and sodium ethoxide in the presence of alcohol and benzene into the *meta*-cyclic *thioether*,  $C_6H_4{<}\begin{matrix}S·CH_2·C_6H_4·CH_2·S\\S·CH_2·C_6H_4·CH_2·S\end{matrix}{>}C_6H_4$, colourless needles, m. p. 235°. H. W.

Formation of Pyrrole Derivatives from Amides of β-Diketonic Esters. W. Küster and P. Schlack [with E. Erfle and W. Heess] (*Ber.*, 1924, **57**, [*B*], 409—413).—Dicarbonyl derivatives obtained from oxalic esters are not generally suited to the production of pyrrole derivatives by reason of their strongly acidic character. Attempts are described to obtain more successful results from compounds of this type in which the acidity has been diminished by the introduction of groups containing nitrogen.

Acetylpyruvanilide, $CH_2Ac·CO·CO·NHPh$, pale yellow needles, m. p. 140—141 (cf. Mumm and Bergell, A., 1912, i, 936), is readily converted into the corresponding *nitroso* derivative, $C_{11}H_{10}O_4N_2$, dark yellow prisms, m. p. 138°, which could not be caused to react with ethyl acetoacetate to yield a substituted pyrrole. A negative result was also obtained when the diketone and ethyl nitrosoacetoacetate were employed.

Ethyl oxalate condenses with acetmethylanilide in the presence of sodium ethoxide to give *ethoxalylacetmethylanilide*,

$$CO_2Et·CO·CH_2·CO·NMePh,$$

colourless needles, m. p. 75°, b. p. 112°/740 mm. (*copper* salt, $C_{26}H_{28}O_8N_2Cu$, m. p. 112—115°; and *iron* salt, $C_{39}H_{42}O_{12}N_3Fe$). Reduction of a mixture of ethyl nitrosoacetoacetate and ethoxalylacetmethylanilide by zinc dust and glacial acetic acid leads to the formation of *ethyl* 3-*carboxyphenylmethylamido*-4-*methylpyrrole*-2 : 5-*dicarboxylate*,  $\begin{matrix}C(CO·NMePh){:}C(CO_2Et)\\ CMe{=\!=\!=}C(CO_2Et)\end{matrix}{>}NH$, colourless crystals, m. p. 82°, which is hydrolysed to the corresponding dicarboxylic *acid*, m. p. 126°.

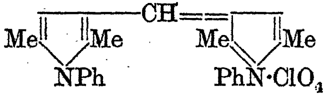
The acid character of ethyl acetylpyruvate, $CH_2Ac·CO·CO_2Et$, is demonstrated by its ability to react with precipitated ferric hydroxide to form the *iron* salt, $C_{21}H_{27}O_{12}Fe$, red, rhombic leaflets. H. W.

Synthesis of Cryptopyrrolecarboxylic Acid. (The Synthesis of the Acid Scission Products of Blood Pigment. I.) H. Fischer and B. Weiss (*Ber.*, 1924, **57**, [*B*], 602—609; cf. A., 1922, i, 759; 1923, i, 707; this vol., i, 201).—Cryptopyrrolecarboxylic acid has been synthesised in the following way: ethyl 2 : 4-dimethylpyrrole-3-aldehyde-5-carboxylate was condensed with cyanoacetic acid by means of acetic anhydride to give *ethyl* 2 : 4-*dimethyl*-3-[ω-*cyano*-ω-*carboxyvinyl*]*pyrrole*-5-*carboxylate* (yellow needles, m. p. 239°). The latter on reduction gave *ethyl* 2 : 4-*dimethyl*-3-[ω-*cyano*-ω-*carboxyethyl*]*pyrrole*, which forms crystals, m. p. 184°; this was then either (i) heated in a vacuum to give *ethyl* 2 : 4-*dimethyl*-3-ω-*cyanoethylpyrrole*-5-*carboxylate* (m. p. 134°), which was then hydrolysed by concentrated alkali, and after acidification, the crude acid heated with acetic acid and hydriodic acid, the product being cryptopyrrolecarboxylic acid; or (ii) the nitrile-carboxylic acid was (by heating with acetic and hydriodic acids) converted into cryptopyrrolecarboxylic acid. The structure of the acid is thus definitely settled. The following new compounds were also prepared: *ethyl* 2 : 4-*dimethyl*-3-ω-*nitrovinylpyrrole*-5-*carboxylate*, from the corresponding aldehyde and nitromethane or nitroacetic acid, is yellow and has m. p. 231—232°; *ethyl* 2 : 4-*dimethyl*-5-ω-*nitrovinylpyrrole*-3-*carboxylate*, m. p. 165°, was prepared from the isomeric aldehyde and nitromethane. *Ethyl* 2 : 4-*dimethyl*-3-[-*cyano*-ω-*carbethoxyvinyl*]*pyrrole*-5-*carboxylate* (the ethyl ester of the nitrile-carboxylic acid), m. p. 239°, was prepared from the same aldehyde and ethyl cyanoacetate in presence of methylamine; it forms white needles, m. p. 165°, and on hydrolysis yields 2 : 4-*dimethylpyrrole*-3-*aldehyde*-5-*carboxylic acid*, m. p. 230° (decomp.). The following compounds were similarly prepared from cyanoacetic ester and the corresponding aldehyde: 2 : 4-*dimethyl*-3-[ω-*cyano*-ω-*carbethoxyvinyl*]*pyrrole*, crystals, m. p. 121°, giving, when hydrolysed, 2 : 4-*dimethylpyrrole*-3-*aldehyde*, m. p. 126°; *ethyl* 2 : 4-*dimethyl*-5-[ω-*cyano*-ω-*carbethoxyvinyl*]*pyrrole*-3-*carboxylate*, yellow crystals, m. p. 153°; 3-*acetyl*-2 : 4-*dimethyl*-5-[ω-*cyano*-ω-*carbethoxyvinyl*]*pyrrole*, yellow crystals, m. p. 174°; 2 : 4 : 5-*trimethyl*-3-[ω-*cyano*-ω-*carbethoxyvinyl*]*pyrrole*, dark yellow crystals, m. p. 147°; *ethyl* 2 : 4-*dimethyl*-3-[ω-*cyano*-ω-*carbethoxyethyl*]*pyrrole*-5-*carboxylate*, white needles, m. p. 131°; *ethyl* 2 : 4-*dimethyl*-3-[*dicyanovinyl*]-*pyrrole*-5-*carboxylate*, m. p. 214°, from 2 : 4-dimethyl-5-carbethoxypyrrole-3-aldehyde and malononitrile in acetic anhydride; *ethyl* 4-*methyl*-3-*propionyl*-2-*ethylpyrrole*-5-*carboxylate*, from nitrosoacetoacetic ester and dipropionylmethane in glacial acetic acid with the addition of zinc dust, white needles, m. p. 112°; 5-*carbethoxy*-2 : 4-*dimethyl*-3-*pyrrylglyoxylic ester*, m. p. 133°, was prepared from ethyl 2 : 4-dimethylpyrrole-5-carboxylate and methyl cyanocarbonate in presence of hydrochloric acid. Ethyl 2 : 4-dimethyl-3-[cyanoacetyl]pyrrole-5-carboxylate reacts with hydrazine hydrate in presence of sodium ethoxide to give an oily *substance* which shows an intense pyrrole reaction; it forms a *picrate*, and an azo *dye*, m. p. 166°.

F. A. M.

Synthetic Experiments with the Fission Products of the Blood Pigments and the Formation of Complex Salts from Dipyrrylmethenes. II. H. Fischer and M. Schubert (*Ber.*, 1924, **57**, 610—617; cf. preceding abstract).—The synthesis of cryptopyrrole has been modified by heating ethyl 2 : 4-dimethyl-3-acetylpyrrole-5-carboxylate with hydrazine hydrate and sodium ethoxide at 180°. In the synthesis of cryptopyrrole-aldehyde by the Gattermann hydrocyanic acid method, *cryptopyrrole-aldimine* (isolated as the *picrate*, yellow crystals, m. p. 205°) is formed. Attempts to hydrolyse the intermediate product in the synthesis (dicryptopyrrylmethylamine) were unsuccessful, the imine, however, readily yielding cryptopyrrole-aldehyde. The amine, with semicarbazide, affords the semicarbazone of the aldehyde. 5-*Chloroacetyl*-2 : 3-*dimethyl*-4-*ethylpyrrole*, from hæmopyrrole and chloroacetonitrile, forms colourless needles, m. p. 140°. 5-*Dimethylaminoacetyl*-2 : 3-*dimethyl*-4-*ethylpyrrole hydrochloride* (colourless needles, m. p. 73°) results from chloroacetylhæmopyrrole and dimethylamine. On submitting hæmopyrrole to the Gattermann synthesis, the product consists of a mixture of *hæmopyrrole-aldimine* (*picrate*, m. p. 200°, decomp. 195—200°), and C-*dihæmopyrrylmethylamine* (*aminodihæmopyrrylmethane*), which forms colourless needles, m. p. 150°. The hæmopyrrole-aldimine, when boiled in aqueous suspension, gives 5-*formyl*-2 : 3-*dimethyl*-4-*ethylpyrrole*, colourless needles, m. p. 85° (*semicarbazone*, colourless crystals, m. p. 195°). The aldehyde, with hot concentrated hydrochloric acid, yields violet-red crystals of bis-[2 : 3-*dimethyl*-4-*ethylpyrryl*]*methene hydrochloride*, m. p. 215°. From phonopyrrolecarboxylic ester (Gattermann synthesis), *methyl hæmopyrrolecarboxylate aldimine hydrochloride* was obtained as colourless needles, m. p. 173°. In a similar manner, cryptopyrrolecarboxylic acid yielded *cryptopyrrolecarboxylic acid aldimine hydrochloride* as colourless needles, m. p. 208°, which on hydrolysis yielded 5-*formyl*-2 : 4-*dimethylpyrrole*-3-*propionic acid*, yellowish-brown needles, m. p. 151° (*semicarbazone*, m. p. 223°). The cryptopyrrolecarboxyaldehyde, on heating with dilute hydrochloric acid, yields red needles of bis-[2 : 4-*dimethyl*-3-*carboxyethylpyrryl*]*methene hydrochloride*, m. p. 235°. Cryptopyrrolecarboxy-aldehyde condenses with cryptopyrrole in presence of hydrochloric acid to give reddish-brown needles of [2 : 4-*dimethyl*-3-*carboxyethylpyrryl*]-[2 : 4-*dimethyl*-3-*ethylpyrryl*]*methene hydrochloride*, m. p. 215°. The following complex salts of *bis*-[2 : 4-dimethyl-3-carbethoxypyrryl]methene were prepared : *copper*, *nickel*, *cobalt*, and *zinc*; the *nickel*, *cobalt*, and *zinc* complex salts of *bis*-[2 : 4-dimethylpyrryl]methene were also made. F. A. M.

Di-β-pyrrylmethenes. I. H. Fischer and K. S. Smeykal (*Ber.*, 1924, **57**, [*B*], 544—550).—The condensation of ethyl 2 : 5-dimethylpyrrole-3-carboxylate with formic acid in presence of perchloric acid affords a substance, $C_{13}H_{17}N_2{\cdot}ClO_4$, orange needles, decomp. 220—230°, and possessing marked sternutatory properties. It appears to be identical with the *perchlorate* of the product obtained by Piloty (A., 1915, i, 461) by condensing 2 : 5-dimethylpyrrole with 3-formyl-2 : 5-dimethylpyrrole, which appears to be *di*-3-(2 : 5-*dimethylpyrryl*)*methene*. It was obtained also by condensing 2 : 5-dimethylpyrrole with formic acid in presence of perchloric acid. The free *base* forms orange needles charring above 200°. The *hydrochloride* forms long, red needles, the *sulphate*, small, reddish-brown needles. Ethyl 1-phenyl-2 : 5-dimethylpyrrole-3-carboxylate condenses with formic acid in presence of perchloric acid to give the *perchlorate* of a substance, $C_{25}H_{25}N_2{\cdot}ClO_4$, presumably *di*-3-(1-*phenyl*-2 : 5-*dimethylpyrryl*)*methene* (annexed formula), which forms reddish-brown leaflets, m. p. 245° (decomp.).



Diethyl 1-hydroxy-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate condenses with formic acid in presence of perchloric acid to give long, red needles of the perchlorate of a substance, decomposing at 210—215°, of the formula $C_{13}H_{17}O_6N_2Cl$, probably the *perchlorate* of di-3-(1-hydroxy-2 : 5-dimethylpyrryl)methene. Ethyl 2 : 5-dimethylpyrrole-4-aldehyde-3-carboxylate undergoes auto-condensation when heated with strong hydrochloric acid to give a *hydrochloride*, red needles, m. p. 181°. The perchlorate, $C_{10}H_{23}N_2{\cdot}ClO_4$, appears to be that of *ethyl* 2 : 5 : 2′ : 5′-*tetramethyldi*-β-*pyridylmethene*-4-*carboxylate*, the base being a yellow powder charring at 220—230°. The mother-liquors contain a small amount of the base previously obtained from ethyl 2 : 5-dimethylpyrrole-3-carboxylate. F. A. M.

Catalytic Hydrogenations under Pressure in the Presence of Nickel Salts. VIII. Compounds of the Indole Series. J. VON BRAUN, O. BAYER, and G. BLESSING (*Ber.*, 1924, 57, [*B*], 392—403).—An extension of previous work (A., 1923, i, 835; this vol., i, 426). Indole resembles quinoline in that hydrogenation takes place primarily in the heterocyclic nucleus. The presence of substituents in this nucleus increases its resistance to reduction, and causes hydrogenation to occur to a greater or less extent in the benzenoid half of the molecule. As in the quinoline series, this tendency can be balanced by the introduction of substituents into the benzenoid nucleus.

Hydrogenation of the indoles was effected in decahydronaphthalene solution, generally at 220—250°. The reaction usually comes to an end before the calculated volume of hydrogen has been absorbed and, when this is the case, ammonia is also formed.

The pyrrole ring is not completely stable under the conditions of hydrogenation and yields fully hydrogenated indoles (see below) and *o*-alkylanilines, among which, *o*-iso*propylaniline*, b. p. 95°/13 mm., d_4^{12} 0·9760 (*hydrochloride*, m. p. 182°; *picrate*, m. p. 160°; *acetyl* derivative, m. p. 70°; *phenylthiocarbamide* compound, m. p. 129—130°), does not appear to have been described previously.

Indole, when hydrogenated at 225° until further absorption of gas does not occur, yields 8% of unchanged material and 66% of basic substances, whereas the remainder suffers more complete degradation accompanied by the production of ammonia. The bases consist of perhydroindole (octahydroindole), a colourless liquid with an odour of hemlock, b. p. 170—171°/760 mm., d_4^{17} 0·8845 [Willstätter and Jacquet (A., 1918, i, 392) give b. p. 182—183°/720 mm., 65°/12 mm., d_4^{21} 0·9947], which yields a chloroplatinate, m. p. 238—239° [Willstätter and Jacquet, m. p. (indefinite) 172—173°]; a *picrate*, m. p. 189—190° (Willstätter and Jacquet, m. p. about 137—138°); a quaternary *iodide*, m. p. 234° (decomp.), and a *benzenesulphonyl* derivative, m. p. 121—122°; also *o*-ethylaniline, b. p. 209—210°/760 mm., d_4^{21} 0·9769 (*hydrochloride*, m. p. 191°; *picrate*, m. p. 194—195°; *acetyl* derivative, needles, m. p. 113°; *benzoyl* derivative, m. p. 146°; *phenylthiocarbamide* compound, needles, m. p. 124°; *benzenesulphonyl* derivative, m. p. 101—102°). 2 : 3-Dihydroindole can readily be prepared by the partial hydrogenation of indole at 180°.

[In part with G. LEMKE.]—2-Methylindole is converted by hydrogen at 220° into a mixture of 2-*methyloctahydroindole* and 2-*methyl*-4 : 5 : 6 : 7-*tetrahydroindole*. The former compound is a colourless liquid with a pronounced basic odour, b. p. 62°/12 mm., d_4^{8} 0·9142; it gives a *picrate*, pale yellow prisms, m. p. 192—193°, and a *benzenesulphonyl* derivative, m. p. 110—112°. The corresponding quaternary *iodide*, m. p. 196°, is decomposed by treatment with silver oxide and subsequent distillation into an apparently homogeneous, unsaturated *base*, $NMe_2{\cdot}C_6H_8{\cdot}CH{:}CHMe$ or $C_6H_9{\cdot}CH_2{\cdot}CHMe{\cdot}NMe_2$, b. p. 80—81°/13 mm., d_4^{15} 0·8603, which yields a *picrate*, m. p. 129—130°, and a quaternary *iodide*, m. p. 187—188°. When the latter compound is treated with silver oxide and the product is distilled, *propenyltetrahydrobenzene*, $C_6H_9{\cdot}CH{:}CHMe$, b. p. 161°, d_4^{17} 0·8285, $n_D^{17{\cdot}6}$ 1·4837, is obtained. 2-Methyl-4 : 5 : 6 : 7-tetrahydropyrrole is a colourless liquid, b. p. 105°/13 mm., d_4^{10} 0·9871, which gives all the reactions characteristic of pyrroles.

3-Methylindole yields 3-*methyl*-4 : 5 : 6 : 7-*tetrahydroindole*, b. p. 105°/12 mm., d_4^{14} 0·9698, and 3-*methyloctahydroindole*, a mobile liquid, b. p. 70°/12 mm., d_4^{8} 0·8908 [*hydrochloride*, m. p. 260° (decomp.); *picrate*, m. p. 195—196°; *quaternary iodide*, $C_{11}H_{22}NI$, m. p. 190°; *benzenesulphonyl* derivative, colourless crystals, m. p. 129—130°].

1 : 2-Dimethylindole is rapidly hydrogenated at 200° to a mixture of somewhat unstable 1 : 2-*dimethyl*-4 : 5 : 6 : 7-*tetrahydroindole*, b. p. 108°/12 mm., d_4^{20} 0·9815, and 1 : 2-*dimethyloctahydroindole*, a colourless liquid with an odour of hemlock, b. p. 71°/12 mm., d_4^{20} 0·8822, which suffers partial dehydrogenation when boiled. It yields a methiodide, m. p. 197° (also obtained from 2-methyloctahydroindole), a very hygroscopic *hydrochloride*, a *chloroplatinate*, decomp. 220°, and a *picrate*, m. p. 149—150°.

2 : 5-Dimethylindole is slowly and incompletely hydrogenated at 250°. It gives small amounts of 2 : 5-dimethyloctahydroindole, which is characterised as the *benzenesulphonyl* derivative, m. p. 114°, and, preponderatingly, o-*propyl*-p-*toluidine*, a colourless liquid, b. p. 98—99°/13 mm., d_4^{12} 0·9666. The latter substance gives a *benzenesulphonyl* derivative, m. p. 104°, a *picrate*, m. p. 201°, a *hydrochloride*, m. p. 195°, a *benzoyl* derivative, m. p. 174—175°,

and a *phenylthiocarbamide* compound, m. p. 146°; the amine is converted by boiling its diazotised solution into o-*propyl*-p-*cresol*, b. p. 97°/13 mm., d_4^{22} 1·018.

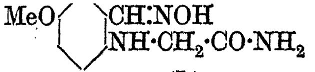
2 : 4 : 7-*Trimethylindole*, a colourless liquid which rapidly darkens in colour, b. p. 158—159°/13 mm., is prepared by the condensation of *p*-xylylhydrazine with acetone and treatment of the product with zinc chloride at 160°. It is hydrogenated to 2-*propyl*-3 : 6-*dimethylaniline*, b. p. 107—110°/13 mm., d_4^{21} 0·9680. The corresponding *picrate*, m. p. 184°, the non-crystalline *hydrochloride*, and the brownish-yellow *chloroplatinate*, decomp. 178°, are described.

H. W.

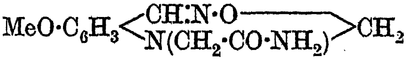
The Methoxyindoles and their Derivatives. K. G. Blaikie and W. H. Perkin, jun. (*J. Chem. Soc.*, 1924, **125**, 296—335).—2-Nitro-5-, -3-, and -6-methoxytoluenes were condensed with ethyl oxalate in presence of potassium ethoxide to form the corresponding nitromethoxyphenylpyruvic acids. 2-*Nitro*-5-*methoxyphenylpyruvic acid* forms yellow needles, m. p. 128°, and gives a *phenylhydrazone*, yellow prisms, m. p. 151—152° (decomp.). 2-*Nitro*-3-*methoxyphenylpyruvic acid* crystallises from acetic acid in yellow prisms, m. p. 118—145°, containing the solvent, which is lost at 100°, leaving the acid as an opaque, pale yellow powder, m. p. 161—162°. The *phenylhydrazone* forms yellow needles, m. p. 159° (decomp.). 2-*Nitro*-6-*methoxyphenylpyruvic acid* forms yellow, indefinite crystals containing benzene, m. p. 47—55°, which retain the solvent after several days in a vacuum. The *phenylhydrazone* forms yellow needles, m. p. 173—174° (decomp.). On oxidation with alkaline hydrogen peroxide, the above nitromethoxyphenylpyruvic acids yield, respectively, 2-*nitro*-5-*methoxyphenylacetic acid*, faintly brown needles, m. p. 176°; 2-*nitro*-3-*methoxyphenylacetic acid*, colourless needles, m. p. 137—138°; and 2-*nitro*-6-*methoxyphenylacetic acid*, bright yellow needles, m. p. 172°. On reduction with ammoniacal ferrous sulphate, the nitromethoxyphenylpyruvic acids give good yields, respectively, of 5-*methoxyindole*-2-*carboxylic acid*, colourless needles, m. p. 196—197° (decomp.) (*ethyl* and *methyl* esters, colourless needles, m. p. 156° and 177°, respectively); 7-*methoxyindole*-2-*carboxylic acid*, colourless needles, m. p. 182° (decomp. at 220—225°) (*ethyl* ester, flat, colourless needles, m. p. 114°; *methyl* ester, colourless plates, m. p. 129°); and 4-*methoxyindole*-2-*carboxylic acid*, colourless needles, m. p. 234—235° (decomp.) (*methyl* ester, colourless plates, m. p. 143·5°; *ethyl* ester, colourless needles, m. p. 161·5°). The above acids lose carbon dioxide on heating, with formation, respectively, of 5-, 7-, and 4-methoxyindoles. 5-*Methoxyindole* forms colourless needles, m. p. 55°, b. p. 176—178°/17 mm., slightly volatile in steam. It forms a *picrate*, $C_{15}H_{12}O_8N_4$, bright red needles, m. p. 145°, and a 1-*acetyl* derivative, colourless, prismatic crystals, m. p. 82°, b. p. 210—211°/25 mm. Two *nitro*-1-*acetyl*-5-*methoxyindoles* (*a*) light brown, flat needles, m. p. 149°, and (*b*) brown plates, m. p. 213—214°, are described, and afford, on hydrolysis, *nitro*-5-*methoxyindoles* (*a*) yellow needles, m. p. 144°, (*b*) m. p. 144° (mixed m. p. 112°), respectively. Application of the Tiemann-

Reimer reaction to 5-methoxyindole produced a mixture of *5-methoxyindole-3-aldehyde*, m. p. 173°, and *3-chloro-6-methoxyquinoline*, m. p. 73—74°. *7-Methoxyindole* forms a colourless syrup, b. p. 157°/17 mm. (*picrate*, $C_{15}H_{12}O_8N_4$, m. p. 156°). *7-Methoxyindole-3-aldehyde*, m. p. 159—160°, *3-chloro-8-methoxyquinoline*, m. p. 84·5°, and *4-methoxyindole*, m. p. 69·5° (*picrate*, m. p. 159—160°), are described.

5-Methoxyindole was also synthesised as follows: 2-amino-5-methoxybenzaldoxime was condensed with chloroacetamide, with formation of *4-methoxy-2-aldehydophenylglycineamide oxime* (I), yellow plates, m. p. 196° (decomp.). The *formyl* derivative (II)



(I.)



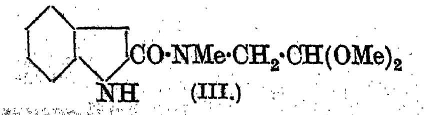
$$\mathrm{MeO{\cdot}C_6H_3}<\begin{matrix}\mathrm{CH{:}N{\cdot}O}\\ \mathrm{N(CH_2{\cdot}CO{\cdot}NH_2)}\end{matrix}>\mathrm{CH_2}$$

(II.)

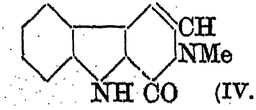
forms bright yellow needles, m. p. 233°. The oxime was hydrolysed to the *oxime* of *4-methoxy-2-aldehydophenylglycine*, pale yellow needles, m. p. 178° (slow decomp.), which was converted by the action of sulphurous acid into *4-methoxy-2-aldehydophenylglycine*, bright orange prisms, m. p. 183° (decomp.) (*phenylhydrazone*, yellow needles, m. p. 175—176°), and this, on heating with sodium acetate and acetic anhydride, yielded 1-acetyl-5-methoxyindole, from which the 5-methoxyindole was obtained on hydrolysis.

α-Ketobutyric acid p-*methoxyphenylhydrazone*, yellow plates, m. p. 105°, yields the *ethyl* ester of *5-methoxyscatole-2-carboxylic acid*, colourless needles, m. p. 151—152°, on treatment with alcoholic sulphuric acid. The free acid forms colourless needles, m. p. 200—201° (decomp.), and the *methyl* ester, colourless plates, m. p. 156°. In the same way, *α-ketobutyric acid* o-*methoxyphenylhydrazone*, pale yellow plates, m. p. 112° (*ethyl* ester, yellow prisms, m. p. 59—60°) is converted into *7-methoxyscatole-2-carboxylic acid*, colourless needles, m. p. 222—223° (decomp.) (*methyl* ester, colourless plates, m. p. 144—145°). The above methoxyscatolecarboxylic acids lose carbon dioxide on heating, with formation, respectively, of *5-methoxyscatole*, plates, m. p. 66° (*picrate*, m. p. 151—152°) and *7-methoxyscatole*, a yellow oil, b. p. 170°/20 mm. (*picrate*, m. p. 156°). The methoxy-indoles and -scatoles give deep colorations with a pine shaving moistened with hydrochloric acid, and characteristic colours, intensified in the case of the indoles by the addition of nitrite, with a solution of *p*-dimethylaminobenzaldehyde in aqueous-alcoholic hydrochloric acid (Ehrlich's reagent).

The action of alcoholic hydrogen chloride on *4-methoxyindole-2-carboxydimethylacetalylmethylamide* (III) (needles, m. p. 112°)



(III.)

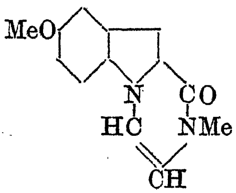


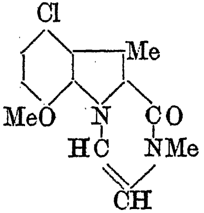
(IV.)

leads to the formation of *9-methoxy-3-keto-4-methyl-3 : 4-dihydro-4-carboline* (IV), needles, m. p. 250°, whilst *5-methoxyindole-2-carb-*

oxydimethylacetalylmethylamide (colourless plates, m. p. 159°) yields about equal proportions of 10-*methoxy*-3-*keto*-4-*methyl*-3 : 4-*dihydro*-4-*carboline*, colourless needles, m. p. 280°, and 10-*methoxy*-5-*keto*-4-*methyl*-4 : 5-*dihydroindolediazine*(1 : 4) (V), colourless, prismatic needles, m. p. 243°.

(V.)





(VI.)

7-*Methoxyindole*-2-*carboxydimethylacetalylmethylamide*, a syrup, yields about 4 parts of 12-*methoxy*-3-*keto*-4-*methyl*-3 : 4-*dihydro*-4-*carboline*, pale yellow plates, m. p. 250°, to 1 part of 12-*methoxy*-5-*keto*-4-*methyl*-4 : 5-*dihydroindolediazine*(1 : 4), four-sided prisms (hydrated), m. p. 135° (anhydrous). 5-*Methoxyindole*-2-*carboxyacetalylamide*, colourless prisms, m. p. 151—152°, yields on the same treatment only 10-*methoxy*-5-*keto*-4:5-*dihydroindolediazine*(1:4) microscopic plates, sintering at 265°, m. p. 280°, whilst 5-*methoxyindole*-2-*carboxyacetalylmethylamide*, colourless needles, m. p. 127°, yields equal quantities of the above carboline (m. p. 280°) and indolediazine (m. p. 243°). The direction of ring formation is thus dependent on the presence or absence of the methyl group in the acetalylamide chain (cf. T., 1922, **121**, 1875). The product derived similarly from 7-methoxyscatole-2-carboxylic acid contained chlorine (apparently introduced in preparing the acid chloride), and was probably 9-*chloro*-12-*methoxy*-5-*keto*-4 : 7-*dimethyl*-4 : 5-*dihydroindolediazine*(1 : 4) (VI), colourless, striated needles, m. p. 109°. It gave no colour reactions with aldehydes.

2-*Nitro*-α-*methoxycinnamic acid*, pale yellow clusters of needles, m. p. 164—165°, is obtained by methylation of the condensation product from *o*-nitrotoluene and ethyl oxalate in presence of sodium ethoxide (*methyl* ester, m. p. 67°). 2-*Amino*-α-*methoxycinnamic acid* loses acetic acid of crystallisation at 100°, forming a pale yellow, opaque powder, m. p. 167° (decomp.) (*methyl* ester, m. p. 60—61°). When treated with cold, concentrated sulphuric acid, boiled with 10% hydrochloric acid, or heated above its m. p., the acid is decomposed into methyl alcohol and indole-2-carboxylic acid. In the same way, by the methylation of metallic derivatives of ethyl nitromethoxyphenylpyruvates, 2-*nitro*-α : 5-*dimethoxycinnamic acid*, yellow needles, m. p. 198—200° (decomp.) (*methyl* ester, m. p. 113—114°; *ethyl* ester, m. p. 74·5°), and 2-*nitro*-α : 3-*dimethoxycinnamic acid*, colourless needles, m. p. 202° (decomp.) are produced. 2-*Amino*-α : 5-*dimethoxycinnamic acid* separates from acetic acid in colourless needles containing the solvent, which is lost at 100°, leaving the acid as a pale yellow, opaque powder, m. p. 173—174° (*methyl* ester, m. p. 81°). 2-*Amino*-α : 3-*dimethoxycinnamic acid* loses acetic acid of crystallisation on standing in air, is then yellow, and has m. p. 139° (decomp.). Both the above amino-acids decompose on heating into methyl alcohol and the corresponding methoxyindole-2-carboxylic acids. Scatole-2-carboxylic acid can be obtained by a similar synthesis from α-keto-β-*o*-nitrophenylbutyrate, but the corresponding methoxy derivatives could not be isolated. F. G. W.

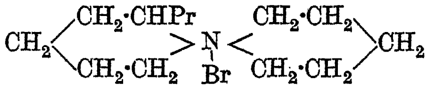
Constitution of Naphtholisatin and its Derivatives. N. Dănăilă (*Bul. Soc. Româna Stiin.*, 1923, **26**, 87—95).—A question of priority in connexion with a paper by Cândea (A., 1923, i, 246; cf. Dănăilă, A., 1916, i, 497, and Dissert., Berlin, 1909). R. B.

Oxidation of Carbazole by Silver Oxide. G. E. K. Branch and W. W. Hall (*J. Amer. Chem. Soc.*, 1924, **46**, 438—445).—In continuation of previous work on this subject, the authors have obtained three fractions B, E, and A (cf. A., 1921, i, 56). E, $C_{36}H_{27}ON_3$ (?), is a white powder, m. p. 189—197° (with charring), which reacts with bromine to give a bromide (?), m. p. 117—125°. It reacts with nitric oxide, and affords two nitroso derivatives, yellow solids, m. p. 216° (decomp.) and 228° (decomp.), respectively. Sulphuric acid converts it into an isomeric *substance*, m. p. 250°. A is a yellow powder affording a bromo derivative, m. p. 85—100°. E is considered to be an hydroxymonocarbazyldibiphenylenehydrazine in which two or three of the carbazole rings are reduced to diphenylamine nuclei, whilst B (which affords a bromo derivative, m. p. 230—245°) is an intermediate in the formation of E, the latter being formed by the combination of the reduced B radicals and the carbazyl nuclei. A. B. S.

The Chemistry of Carbazole. H. Lindemann (*Ber.*, 1924, **57**, [*B*], 555—559).—A method is described for preparing 3-nitrocarbazole from carbazole, using glacial acetic acid, sodium nitrite, and nitric acid. 3-Nitro-9-nitrosocarbazole, first obtained, when hydrolysed with alcoholic 40% potassium hydroxide, gives 3-nitrocarbazole, together with about 4% of an isomeride (1-nitrocarbazole ?) (yellow needles, m. p. 187°); the nitro compound (m. p. 164°), hitherto described as the 1-nitro compound, must therefore be either the 2- or 4-*nitrocarbazole* (cf. A., 1909, i, 961). 3-*Nitro*-N-*methylcarbazole* (yellow needles, m. p. 173°), and 3-*nitro*-N-*ethylcarbazole* (yellow needles, m. p. 128°) were prepared by alkylation of the 3-nitro compound. The nitro-*N*-methyl compound when reduced afforded 3-*amino*-9-*methylcarbazole*, grey needles, m. p. 174°. Its *salts* with mineral acids are soluble in water and give *acetyl* and *benzoyl* derivatives, m. p. 210° and 211°, respectively. 3-*Amino*-N-*ethylcarbazole* forms white needles, m. p. 113—114° (*acetyl* derivative, m. p. 190°; *benzoyl* derivative, m. p. 180°).

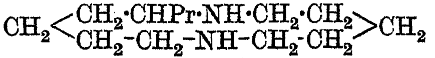
3-Nitro-9-ethylcarbazole, m. p. 128°, does not agree in its properties with the product obtained by Delétra and Ullmann (A., 1904, i, 272) (cf. also Stevens and Tucker, T., 1923, **123**, 2140) from 2-amino-4-nitro-*N*-ethyldiphenylamine; the latter substance, obtained by reducing the corresponding dinitro compound with sodium sulphide, forms red crystals melting at 76°. On treatment with nitrous acid the corresponding diazonium compound, 2(*phenylmethylamino*)5-*nitrophenyldiazonium nitrate*, was obtained in the form of very stable yellow needles exploding at about 118°. All attempts to convert it into 3-nitro-*N*-methylcarbazole were unsuccessful. F. A. M.

Cyclic bis-Imines and their Decomposition. IV. J. VON BRAUN and J. POHL (*Ber.*, 1924, **57**, [*B*], 480—484).—Coniine (2 mols.) and αε-dibromopentane interact at water-bath temperatures to give a solid product, probably in accordance with the equation: $2C_8H_{16}>NH+Br[CH_2]_5Br=C_8H_{16}>N\cdot HBr+C_8H_{16}N[CH_2]_5Br$. On further warming there results the hygroscopic quaternary *bromide*, $C_{13}H_{26}NBr$ (I), m. p. 228°. The latter, when heated with ammonia at 200°, is partly converted into the *bis-imine* (II), a colourless oil, b. p. 145—146°/11 mm., d_4^{18} 0·89.



$$CH_2<\begin{matrix}CH_2\cdot CHPr\\CH_2\cdot CH_2\end{matrix}>\underset{Br}{N}<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH_2$$

(I.)

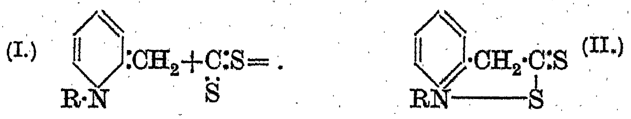


$$CH_2<\begin{matrix}CH_2\cdot CHPr\cdot NH\cdot CH_2\cdot CH_2\\CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\end{matrix}>CH_2$$

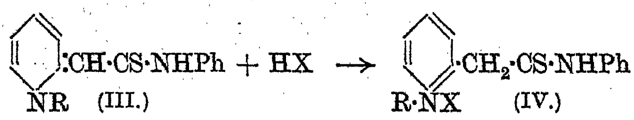
(II.)

The *picrate*, *hydrochloride*, and *chloroplatinate* are oily. The *dimethiodide* yields a solid *chloroplatinate*, m. p. 248°. A 40-g. frog is completely paralysed by 0·005 g. of the bis-imine in 3—4 minutes, whilst the same dose of coniine requires about 39 minutes to produce paralysis. F. A. M.

Reactions of *N*-Alkyl-methylenedihydro-pyridines and -quinolines. W. SCHNEIDER, K. GAERTNER, and A. JORDAN (*Ber.*, 1924, **57**, [*B*], 522—532; cf., A. 1921, i, 878).—*N*-Alkyl-α-(or γ-)methylenepyridanes (cf. Decker, A., 1905, i, 667), which are formed on treating quaternary salts of α- or γ-methylated pyridines or quinolines with alkali, are capable of combining directly with either carbon disulphide, phenylcarbimide, or phenylthiocarbimide to form crystalline products. In the case of α-picoline alkiodides, it is suggested that the methylene base (I) reacts thus:



so that the product (II) would be the betaine of *N*-alkyl-α-pyridyldithioacetic acid; whilst the thiocarbimide additive product of the methylene base would have the structure (III) and its salts the



structure (IV), the carbimide additive compounds having analogous formulæ which would agree with the ready oxidation of both sulphur and oxygen compounds by cold neutral permanganate, whilst in acid solution they are only slowly oxidised.

N-Methyl-α-methylenedihydropyridine was prepared by treating α-picoline methosulphate with alkali and extracting with ether; on treating the yellow ethereal solution with carbon disulphide, yellow leaflets of the *additive* compound, $C_8H_9NS_2$, were formed which charred at 175° and had m. p. 186°. The *phenylthiocarbimide* (III) forms dark red crystals, m. p. 153°. It is soluble in dilute acids to give pale yellow solutions of the salts (IV), from which the compound is reprecipitated by alkalis. The *hydriodide* forms colourless needles, m. p. 160°, the *picrate*, yellow needles, m. p. 156°. The *phenylcarbimide* forms yellow needles, m. p. 172° (*picrate*, yellow needles, m. p. 173°). N-*Ethyl-α-methylenedihydropyridine* gave the following derivatives: *carbon disulphide additive* compound, yellow leaflets, char at 170°, m. p. 180°; *phenylthiocarbimide*, dark red crystals, m. p. 143°; *hydriodide*, m. p. 177°, *picrate*, m. p. 113°; *phenylcarbimide*, needles, m. p. 172°. N-*Benzyl-α-methylenedihydropyridine* (from α-picoline benzochloride) gave the following derivatives: *phenylthiocarbimide*, red crystals, m. p. 189°; *picrate*, m. p. 150°; *phenylcarbimide*, yellow crystals, m. p. 192°; *picrate*, m. p. 126°. The following are derivatives of *methylene-anhydro bases from* s-*collidine alkiodides:* (i) *methiodide*: *phenylthiocarbimide*, yellowish-brown crystals, m. p. 185°; *phenylcarbimide*, yellow, m. p. 188°; (ii) *ethiodide*: *phenylthiocarbimide* compound, yellowish-brown, m. p. 190°; *phenylcarbimide*, bright yellow, m. p. 198°. The following derivatives of N-*methyl-γ-methylenedihydropyridine* (from γ-picoline methiodide) are described: *phenylthiocarbimide*, brown leaflets, m. p. 218°; *phenylcarbimide*, yellow needles, m. p. 196°. The *pseudo*-bases from pyridine methiodide and from β-picoline methiodide gave no recognisable crystalline products with either phenylcarbimide or thiocarbimide. N-*Methyl-α-methylenedihydroquinoline* with carbon disulphide gave no definite product but the following are described: *phenylthiocarbimide*, coppery leaflets, m. p. 170°; *hydriodide*, pale yellow, m. p. 192°; *perchlorate*, yellowish-brown, m. p. 188—190°; *picrate*, yellow, m. p. 168—169°; *phenylcarbimide*, yellow crystals, m. p. 173°; *hydriodide*, yellow, m. p. 190—191°; *perchlorate*, colourless, m. p. 199°; *picrate*, m. p. 168—169°. Derivatives of N-*ethyl-α-methylenedihydroquinoline* are: *phenylthiocarbimide*, reddish-brown crystals, m. p. 162°; *phenylcarbimide*, yellow needles, m. p. 167°. Derivatives of *methylene-anhydro base from α:γ-dimethylquinoline ethiodide* are: *phenylthiocarbimide*, reddish-brown needles, m. p. 145°; *phenylcarbimide*, yellow needles, m. p. 207°. Crystalline *additive* compounds were also obtained from the base derived from lepidine ethiodide, but were not examined further. Experiments were carried out also with the *pseudo*-bases derived from 2-ethylquinoline ethiodide, 4-ethylquinoline ethiodide, α-*iso*propylquinoline ethiodide, and quinoline ethiodide itself, but no crystalline additive compounds could be obtained.

F. A. M.

Arylated Pyridines. IV. *N*-Alkylquinopyridanes. W. Dilthey, C. Ammon, and A. Ebert (*J. pr. Chem.*, 1924, [ii], **107**, 7—15; cf. A., 1921, i, 735; 1922, i, 272).—The arylated quinopyridanes obtained by the action of ammonia on the *N*-arylpyridinium salts formed from primary amines and *p*-hydroxylarylpyrylium salts are considered to possess a quinoid structure in the yellowish-red anhydro bases and a benzenoid structure in their bright yellow salts and hydrates. The additive compounds of the bases with benzene are also assigned a quinoid structure. The following individual compounds are described: 1 : 2 : 6-*triphenyl*-4-p-*hydroxyphenylpyridinium chloride*, $C_{29}H_{22}ONCl,0\cdot5HCl$, bright yellow crystals, m. p. 335°, was obtained from 2 : 6-diphenyl-4-*p*-hydroxyphenylpyrylium chloride and aniline (cf. A., 1922, i, 272), and on heating in a xylene bath this gives the dark yellow, neutral *chloride*, $C_{29}H_{22}ONCl$. The two chlorides behave very differently with alcoholic ammonia. The hydrochloride yields a very stable meriquinoid *salt*, $C_{58}H_{43}O_2N_2Cl$, m. p. about 295—300°, from which chlorine is removed quantitatively only by boiling with silver hydroxide. The neutral chloride, in the same way, is converted into a *dihydrate* of the anhydro base, 1 : 2 : 6-*triphenyl*-4-*quino*-1 : 4-*dihydropyridine*. The dihydrate, yellow plates, darkens at 120—130°, melting twice between this temperature and 263°. When dehydrated, the dihydrate affords the orange monohydrate, from which the dark red anhydro base (yellow *picrate* and *nitrate*) is obtained, this, when heated, behaving similarly to the dihydrate, melting first at 175° and then, after solidifying, at 263° to a dark red fluid. With benzene, an *additive* compound, $C_{29}H_{21}ON,C_6H_6$ is formed, as fine, red needles, these, on heating at 110°, giving the anhydro base. Similarly, 2 : 6-diphenyl-4-*p*-hydroxyphenylpyrylium chloride, on heating with *p*-toluidine, gives 2 : 6-*diphenyl*-4-p-*hydroxyphenyl*-1-p-*tolylpyridinium chloride*, bright yellow plates (+$2H_2O$; the water is lost at 100—130°, giving the anhydrous compound, m. p. 343—345°). The *nitrate* is yellow, m. p. 168° (decomp.). With alcoholic ammonia, the chloride yields a *dihydrate* of the anhydro base, yellowish-red needles, which lose their water at 100—130°, giving the anhydro base, 2 : 6-*diphenyl*-1-p-*tolyl*-4-*quino*-1 : 4-*dihydropyridine*, reddish-violet, m. p. 293°. The anhydro base forms an insoluble *additive* compound with benzene, $C_{30}H_{23}ON,C_6H_6$.

From the reaction product of 4 : 6-diphenyl-2-*p*-hydroxyphenylpyrylium iodide and β-naphthylamine in benzene solution, the *picrate*, yellow, m. p. 162—163°, and *perchlorate*, yellow, m. p. 177—178°, of 4 : 6-diphenyl-2-*p*-hydroxyphenyl-1-β-naphthylpyridine were isolated. R. B.

5 : 6 : 7 : 8-Tetrahydroquinolines and their Derivatives. IV. J. von Braun, W. Gmelin, and A. Petzold (*Ber.*, 1924, **57**, [*B*], 382—391; cf. von Braun, Gmelin, and Schultheiss, A., 1923, i, 835).—Further examples are cited which confirm the previous conclusion that the presence of alkyl substituents, according to their number and weight, in the pyridine half of the quinoline molecule inhibits to a greater or less extent the introduction of hydrogen atoms in the presence of nickel into the 1 : 2 : 3 : 4-positions and favours the production of 5 : 6 : 7 : 8-derivatives. The maximum effect is observed in the case of 2 : 3 : 4-trimethylquinoline, which, in complete contrast to quinoline itself, is hydrogenated exclusively in the benzenoid nucleus. The introduction of alkyl groups into the 5 : 6 : 7 : 8-positions exerts an opposite effect. The observations are explained by the hypothesis that the quinoline derivatives are equilibrium mixtures of two forms (benzenoid and centric structures alternating in each nucleus); in extreme cases of loading with substituents, only one variety is present.

2-Propylquinoline dissolved in decahydronaphthalene is converted by hydrogen in the presence of nickel at 170° into a mixture of 2-*propyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (65%) and 2-*propyl*-5 : 6 : 7 : 8-*tetrahydroquinoline* (35%). The former compound is a colourless liquid, b. p. 140—141°/10 mm. (*hydrochloride*, m. p. 221°; *benzoyl* derivative, microscopic crystals, m. p. 101°), whereas the latter base is a colourless liquid with a pronounced odour of pyridine, b. p. 130—132°/11 mm. (the non-crystalline *hydrochloride*, the *chloroplatinate*, decomp. 62°, and the *picrate*, yellow needles, m. p. 119°, are described). 2-*Propyldecahydroquinoline*, obtained in almost quantitative yield by the reduction of 2-propyl-5 : 6 : 7 : 8-tetrahydroquinoline with sodium and alcohol, has b. p. 123—125°/20 mm.; it somewhat resembles coniine in physiological activity. It yields a non-crystalline *nitroso* derivative, an extremely hygroscopic *hydrochloride*, and a *picrate*, m. p. 134—135°.

4-Phenyl-2-methylquinoline gives 4-phenyl-2-methyl-1 : 2 : 3 : 4-tetrahydroquinoline, m. p. 66—67° (16%), and 4-*phenyl*-2-*methyl*-5 : 6 : 7 : 8-*tetrahydroquinoline*, a viscous liquid, b. p. 181—183°/13 mm. (84%). The latter compound yields a *picrate*, m. p. 186—187°, a non-crystalline *hydrochloride*, and a yellow *chloroplatinate*, decomp. 145—147°.

2 : 3 : 4-Trimethylquinoline, m. p. 92° (65° is recorded in the literature), is prepared in the usual manner from aniline and methylacetylacetone; the *picrate*, m. p. 216°, *hydrochloride*, m. p. 274°, and lemon-yellow *methiodide*, m. p. 260°, are described. When hydrogenated in the presence of nickel at 155—160°, the base yields about 2% of 2 : 3 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydroquinoline, which is identified as the *chloroplatinate* of the corresponding *methochloride*, $C_{25}N_{41}Cl_2N_6Pt$, lustrous, orange-coloured needles, m. p. 176°. The main product of the reduction is 2 : 3 : 4-*trimethyl*-5 : 6 : 7 : 8-*tetrahydroquinoline*, a liquid with an odour resembling that of pyridine, b. p. 145—147°/13 mm., which yields a crystalline *dihydrate*, m. p. 31—32°; the *picrate*, m. p. 147°, *hydrochloride*, m. p. 174°, and *methiodide*, m. p. 125—126°, are described. The base is reduced by sodium and alcohol to 2 : 3 : 4-*trimethyldecahydroquinoline*, a colourless liquid with a pronounced odour of hemlock, b. p. 115°/13 mm.; the non-crystalline *nitroso* derivative, the *hydrochloride*, and the *product*, $C_{14}H_{25}NI$ (obtained by exhaustive methylation), a crystalline powder, m. p. 227° after softening at 218°, are described.

2 : 6-Dimethylquinoline readily undergoes catalytic hydrogenation at 105°, yielding 2 : 6-dimethyl-5 : 6 : 7 : 8-tetrahydroquinoline (1·5%) (*picrate*, m. p. 127°; *chloroplatinate*, $C_{22}H_{32}N_2Cl_6Pt$, an orange-coloured powder, decomp. 185°), and 2 : 6-dimethyl-1 : 3 : 2 : 4-tetrahydroquinoline (98·5%), b. p. 133°/12 mm., m. p. 32° (*benzoyl* derivative), m. p. 103°.

Acetylacetone and *p*-xylidine readily yield the corresponding *xylidide*, $C_{13}H_{17}ON$, b. p. about 170°/12 mm., m. p. 41°, which with concentrated sulphuric acid gives 2 : 4 : 5 : 8-*tetramethylquinoline*, a pale yellow, crystalline mass, m. p. 48°, b. p. 168—172°/12 mm.; the base exhibits a pronounced, bluish-violet fluorescence in acid solution. The *hydrochloride*, m. p. 254° after sintering at 243°, and the *picrate*, small needles, m. p. 161°, are described; the methiodide could not be obtained. The base is hydrogenated at 160—170° to a mixture of 2 : 4 : 5 : 8-*tetramethyl*-5 : 6 : 7 : 8-*tetrahydroquinoline* (4%), a colourless liquid, b. p. 135—137°/12 mm. (the non-crystalline *hydrochloride*, the *chloroplatinate*, coarse crystals which blacken above 196°, and the *picrate*, m. p. 131°, are described), and 2 : 4 : 5 : 8-*tetramethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (96%), b. p. 143—145°/12 mm. (the non-crystalline *benzoyl* derivative, the *hydrochloride*, m. p. 211°, and the *picrate*, m. p. 160°, are described).

[With K. Müncker.]—Tetrahydro-α-naphthylamine reacts readily with acetylacetone to yield the *compound* $C_{10}H_{11}N{:}CMe{\cdot}CH_2{\cdot}Ac$, a viscous liquid, b. p. 208°/15 mm., which with concentrated sulphuric acid gives 2 : 4-*dimethyl*-7 : 8 : 9 : 10-*tetrahydro-α-naphthaquinoline*, b. p. 196—200°/15 mm., m. p. 49° (*hydrochloride*, m. p. 243°; *picrate*, m. p. 201°; *methiodide*, m. p. 254°). The catalytic hydrogenation of the base proceeds with unusual difficulty; even at temperatures above 200° the action stops prematurely, owing to poisoning of the catalyst. The main product is 2 : 4-*dimethyl*-1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-*octahydro-α-naphthaquinoline*, a viscous liquid, b. p. 190°/16 mm. (*benzoyl* derivative, m. p. 130—131°; *nitroso* compound, m. p. 62°; *hydrochloride*, m. p. 204°; *picrate*, m. p. 130°). The portion of the product which does not react with benzoyl chloride appears to have suffered partial hydrogenation in the central nucleus. The catalytic reduction of 2 : 4-dimethyl-α-naphthaquinoline, m. p. 52°, yields a mixture of unchanged base, 2 : 4-dimethyl-7 : 8 : 9 : 10-tetrahydro-α-naphthaquinoline, and the above octahydro base; the primary change occurs at the extreme benzene nucleus. H. W.

Intramolecular Condensation Reactions of Aminoacetals and Aminoaldehydes. I. Synthesis of Dihydroquinoline and certain Homologues. C. Räth (*Ber.*, 1924, 57, [*B*], 550—555).—If chloro- or bromo-acetal is heated with *o*-toluidine in a closed tube at 260°, 1 : 2-*dihydroquinoline* (90% yield) is obtained as an almost colourless liquid, b. p. 226° (*hydrochloride*, white, crystalline powder, m. p. 214°; *picrate*, yellow, crystalline powder, m. p. 199—200°; *nitroso* derivative, a viscous, yellow oil), and is accompanied by small quantities of the intermediately formed o-*toluidine*-N-*monoacetal*, a viscous substance, b. p. 250—262°. On heating 1 : 2-dihydroquinoline with ethylene chlorohydrin in benzene solution, 1-(β-*hydroxyethyl*)-1 : 2-*dihydroquinoline* is formed as a viscous, pinkish liquid, b. p. 166—168°/11 mm. The *hydrochloride, picrate*, and *methiodide* were obtained only as oils.

In a similar way, β-bromopropionacetal condenses with *o*-toluidine to form 1 : 2-*dihydroquinaldine*, which is a faintly yellow liquid (b. p. 234—240°) affording an oily *nitroso* derivative; the *hydrochloride*, a white, crystalline powder, has m. p. 197—198°; the *picrate*, yellow crystals, m. p. 189—190°. If methyl-*o*-toluidine be used in place of *o*-toluidine, the product is 1-methyl-1 : 2-dihydroquinaldine, b. p. 252—260° (Freund, A., 1906, i, 600; 1909, i, 417); the *hydrochloride* is an oil, the *picrate* yellow rosettes, m. p. 148—150°. As a by-product was obtained α-o-*tolylmethylaminopropaldehyde*, $CH_3\cdot C_6H_4\cdot NMe\cdot CHMe\cdot CHO$, b. p. 283—288°, which forms a *picrate*, m. p. 152—153°. F. A. M.

The Reactivity of the Chlorine Atom in the 2-Position in Quinoline and Quinoline Derivatives. J. TRÖGER and H. MEINECKE (*J. pr. Chem.*, 1923, [ii], **106**, 203—225).—2-Chloroquinoline reacts slowly with sodium benzenesulphinate in presence of alcohol to give 2-*benzenesulphonylquinoline*, colourless needles, m. p. 160°. This compound is unaffected by a short fusion with alkali, prolonged fusion effecting profound decomposition. When heated with dilute hydrochloric acid at 235°, it affords carbostyril, benzenesulphinic acid, and benzene disulphoxide. It forms no double salts. 2-Chloroquinoline does not react with alkali derivatives of thiophenols, but 2-chloro-3-benzenesulphonylquinoline and the sodium derivative of *p*-thioltoluene afford 3-*benzenesulphonylcarbostyril* p-*tolyl thioether*, $C_9H_5N(SO_2Ph)(SC_7H_7)$, colourless needles, m. p. 131° with previous sintering. When 2-chloro-3-benzenesulphonylquinoline is heated in alcoholic solution with sodium benzenesulphinate at 130°, 2 : 3-dibenzenesulphonylquinoline (m. p. 204°) results (cf. A., 1923, i, 368).

2-o-*Toluenesulphonylquinoline* (colourless prisms, m. p. 127°) was prepared by the above method. 2-*Amino*-3-o-*toluenesulphonylquinoline* (from *o*-toluenesulphonylacetonitrile and *o*-aminobenzaldehyde), white prisms, m. p. 179·5° (*hydrochloride*,

$$C_{16}H_{14}O_2N_2S,HCl,H_2O,$$

white crystals), is converted by nitrous acid into 3-o-*toluenesulphonylcarbostyril*, yellow prisms, m. p. 270°, this substance, with phosphorus pentachloride, affording 2-*chloro*-3-o-*toluenesulphonylquinoline*, colourless needles, m. p. 161°.

From the last-named chloro compound, 3-o-*toluenesulphonylcarbostyril* p-*tolyl thioether* (white crystals, m. p. 191°), 3-o-*toluenesulphonyl*-2-*benzenesulphonylquinoline* (colourless prisms, m. p. 260°), and 3-o-*toluenesulphonylcarbostyril phenyl thioether* (colourless needles, m. p. 154°) were obtained. The last-named ether, on oxidation, affords 3-*o*-toluenesulphonylcarbostyril.

Sodium *p*-toluenesulphinate reacts less rapidly than the benzenesulphinate with 2-chloroquinoline, 2-p-*toluenesulphonylquinoline* (white crystals, m. p. 141°) resulting. Other compounds in this series are: 3-p-*toluenesulphonylcarbostyril* p-*tolyl thioether*, colourless crystals, m. p. 195°; 3-p-*toluenesulphonyl*-2-p-*toluenesulphonylquinoline*, colourless needles, m. p. 184—185°; and 3-p-*toluenesulphonylthiocarbostyril*, lemon-yellow powder, m. p. 226°.

2-p-*Chlorobenzenesulphonylquinoline* forms white needles, m. p. 190°; 3-p-*chlorobenzenesulphonylcarbostyril phenyl thioether* (yellow needles, m. p. 149°) is formed together with some 3-*p*-chlorobenzenesulphonylcarbostyril when 2-chloro-3-*p*-chlorobenzenesulphonylquinoline reacts with sodium thiophenoxide, and on oxidation affords 3-p-*chlorobenzenesulphonyl*-2-*benzenesulphonylquinoline*, white crystals, m. p. 264° (sintering at 250°).

3-p-*Chlorobenzenesulphonylcarbostyril* p-*tolyl thioether*, colourless needles, m. p. 147°, cannot be oxidised to the corresponding disulphone. 2-p-*Bromobenzenesulphonylquinoline* forms white needles, m. p. 145°. 2-*Amino*-3-p-*bromobenzenesulphonylquinoline*, lemon-yellow needles, m. p. 223°, forms a *hydrochloride*, needles, m. p. 256° (decomp.), *nitrate*, yellow, crystalline powder, m. p. (indef.) 105—224°, and *chloroplatinate*, yellowish-red crystals, and is converted by nitrous acid into 3-p-*bromobenzenesulphonylcarbostyril*, yellow needles, m. p. 269°. The last-named substance is converted by phosphorus pentachloride into 2-*chloro*-3-p-*bromobenzenesulphonylquinoline*, colourless needles, m. p. 181·5°. The following were also prepared: 3-p-*bromobenzenesulphonylcarbostyril ethyl ether*, colourless needles, m. p. 156°; 3-p-*bromobenzenesulphonylthiocarbostyril*, yellow crystals, m. p. 254°, and 3-p-*bromobenzenesulphonylcarbostyril* p-*tolyl thioether*, white needles, m. p. 159°.

2-β-*Naphthalenesulphonylquinoline* forms colourless stars, m. p. 137°. 2-*Amino*-3-β-*naphthalenesulphonylquinoline*, yellow needles, has m. p. 180° and forms a *hydrochloride*, yellow needles, m. p. 250° (with previous decomp.), and a *nitrate*, white needles. 3-β-*Naphthalenesulphonylcarbostyril* forms yellow needles, m. p. 294°; 2-*chloro*-3-β-*naphthalenesulphonylquinoline*, yellow crystals, has m. p. 159°; 3-β-*naphthalenesulphonylcarbostyril ethyl ether* forms yellow needles, m. p. 121°; 3-β-*naphthalenesulphonylcarbostyril* p-*tolyl thioether*, silver crystals, has m. p. 176° and oxidises irregularly.

2-o-*Anisolesulphonylquinoline* forms rhombs, m. p. 134°. 2-*Amino*-3-o-*anisolesulphonylquinoline*, colourless crystals, has m. p. 239°, and was converted into 3-o-*anisolesulphonylcarbostyril*, yellow crystals, m. p. 250°. 2-*Chloro*-3-o-*anisolesulphonylquinoline*, quadratic crystals, m. p. 171°, was converted into 3-o-*anisolesulphonylcarbostyril phenyl thioether*, colourless rhombohedra, m. p. 160°, and into 3-o-*anisolesulphonylthiocarbostyril*, yellow crystals, m. p. 233° (*methyl* ether, colourless crystals, m. p. 150°).

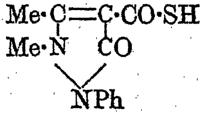
2-p-*Phenetolesulphonylquinoline*, white leaflets, has m. p. 133·5°. 2-*Amino*-3-p-*phenetolesulphonylquinoline* forms yellow leaflets, m. p. 178° [*hydrochloride*, needles, m. p. 233° (decomp.)], and was converted into 3-p-*phenetolesulphonylcarbostyril*, yellow needles, m. p. 241°. 2-*Chloro*-3-p-*phenetolesulphonylquinoline*, yellow crystals, m. p. 162°, was converted into 3-p-*phenetolesulphonylcarbostyril* p-*tolyl thioether*, colourless needles, m. p. 141°, the last-named substance affording, on oxidation, 3-p-*phenetolesulphonyl*-2-p-*toluenesulphonylquinoline*, needles, m. p. 249° (sintering at 239°). 3-p-*Phenetolesulphonylthiocarbostyril*, yellow needles, has m. p. 142°.

From the above it is seen that in 2-chloroquinoline, the chlorine atom cannot be displaced by the ·SR radical, whereas the presence of the grouping $\cdot SO_2R$ in position 3 (especially if R is a *p*-tolyl radical) facilitates the displacement. Again, whilst 2-amino-β-arylsulphonylquinolines (monoacidic bases) cannot be diazotised, the amino radical can readily be displaced by hydroxyl, using nitrous acid. E. E. T.

Carbithionic and Thionic Acid Derivatives of Pyrazolones. E. BENARY and A. SCHMIDT (*Ber.*, 1924, 57, [*B*], 517—522).—By the action of chlorocarbonic ester, or ethyl bromide, on antipyrine in carbon disulphide solution, a product is obtained according to the equation :

$$C_{11}H_{11}ON_2+EtBr+CS_2=C_{11}H_{11}ON_2\cdot CS\cdot SEt+HBr.$$

Since the new substance does not give the typical nitroso reaction of antipyrine, it is assumed that the group –CS·SEt has occupied position 4 and that the substance is *ethyl* 1-*phenyl*-2 : 3-*dimethylpyrazolone*-5-*carbithionate* (cf. Houben, A., 1906, i, 847). It forms orange leaflets, m. p. 178·5—179°, gives no nitroso compound with nitrous acid, and forms an intense red precipitate with bromine in chloroform solution. When treated with alcoholic potassium hydroxide, it affords ethyl mercaptan and 1-*phenyl*-2 : 3-*dimethylpyrazolone*-5-*thionic acid*, sulphur-yellow needles, m. p. 81—82° (annexed formula) (*potassium* and *silver* salts described). The *methyl* ester, yellow needles ($+1\cdot5H_2O$) has m. p. 95° (anhydrous ester, m. p. 113—114°). The following were made in a similar manner from the appropriate substance, ethyl bromide, and aluminium chloride in carbon disulphide solution.



Ethyl 1-*phenyl*-3-*methyl*-5-*pyrazolone*-4-*carbithionate*, from 1-methyl-3-phenyl-5-pyrazolone, forms greenish-yellow prisms, m. p. 81—82°. *Ethyl* 3-*methyl*-5-*pyrazolone*-4-*carbithionate*, orange prisms or needles, m. p. 186°, which with alkali yields 3-methyl-5-pyrazolone; on treating the alkaline solution from the hydrolysis with methyl sulphate, white or pale yellow needles (m. p. 115·5°) are formed, of *methyl* 1 : 2 : 3-(or 1 : 2 : 5-)*trimethyl*-5-*pyrazolone*-4-*carbithionate*. *Ethyl* 5-*pyrazolone*-4-*carbithionate*, from 5-pyrazolone, forms reddish-brown prisms, m. p. 184—185°. *Ethyl* 1-*phenyl*-5-*methyl*-3-*pyrazolone*-4-*carbithionate* forms orange-yellow leaflets, m. p. 114°. From thiopyrine a yellow, crystalline *substance*, m. p. 166°, probably the corresponding carbithionic acid, was obtained. F. A. M.

Dipyridyls from Pyridine. C. R. SMITH (*J. Amer. Chem. Soc.*, 1924, 46, 414—419).—The author describes the preparation and separation of 2 : 2-, 3 : 3-, 3 : 4-, and 4 : 4-dipyridyls. 3 : 4-*Dipyridyl* (plates, m. p. 61°, b. p. 297°) forms a *dihydrochloride*, *mercurichloride,* and *chloroplatinate* and is distinguished from its isomerides by certain colour reactions. On oxidation with potassium permanganate, it affords nicotinic and *iso*nicotinic acids. In the interaction of sodium and pyridine in presence of dry oxygen, the proportions of the various isomerides produced depend on the time, temperature, and pressure conditions. A. B. S.

The Constitution of the Products arising from the Condensation of o-Aminoazo Compounds with Aldehydes. II. OTTO FISCHER (*J. pr. Chem.*, 1924, [ii], **107**, 16—49; cf. A., 1922, i, 956).—A further series of *N*-substituted iminazoles, some already known, has been obtained by the condensation of *o*-aminoazo compounds with aldehydes, and the reduction of these with hydriodic acid is described, the products being a benziminazole and an amine. The condensation products of chrysoidine and aldehydes are shown to be derivatives of 1-anilino-2-phenyl-5-aminobenziminazole. The action of benzyl chloride on *o*-aminoazo compounds did not give the expected *N*-aryldihydrobenziminazoles, but their decomposition products, *e.g.*, aniline and 2-phenylnaphthiminazole. If the benzyl group is introduced into the amine prior to coupling, the azo dyes formed easily decompose in a similar way.

[With E. THIEL.]—From benzeneazo-β-naphthylamine, the following compounds have been prepared. With acetaldehyde, 1-anilino-2-methylnaphthiminazole [yellow *picrate,* m. p. 234°; yellow *nitrosoamine,* decomp. 124°; *acetyl* compound, m. p. 230° (decomp.)]. With methyl iodide in benzene solution it gives a *methyl* base, lustrous, colourless plates, m. p. 195° (*hydrochloride,* m. p. 250°), which does not form a nitrosoamine. With *o*-chlorbenzaldehyde, 1-*anilino*-2-o-*chlorphenylnaphthiminazole,* colourless, tufted needles, m. p. 231° [*picrate,* m. p. 192° (decomp.)]. With salicylaldehyde, 1-*o*-hydroxyanilino-2-phenylnaphthiminazole [golden-yellow *nitrosoamine, diacetyl* compound, m. p. 169° (decomp.)], an intermediate compound, violet-tinged needles, $C_{23}H_{17}ON_3$, being isolated which goes over into the colourless iminazole at 100—110°. With *p*-hydroxybenzaldehyde, 1-*anilino*-2-p-*hydroxyphenylnaphthiminazole,* colourless crystals, m. p. 233° (decomp.) (*nitrosoamine,* decomp. 200°, *diacetyl* compound, prisms, m. p. 224°).

[With F. STAUBER and W. HILD.]—When heated with hydriodic acid (*d* 1·7) under pressure, the *N*-arylbenziminazoles and naphthiminazoles are converted into the corresponding primary amine and iminazole. The iminazoles are not further decomposed even at 180—200°. The following compounds have been prepared.

From *o*-aminoazo-*p*-toluene and benzaldehyde, 1-*p*-toluidino-2-phenyl-5-methylbenziminazole, which on reduction yields *p*-toluidine and 2-*phenyl*-5-*methylbenziminazole,* dense white crystals, m. p. 240°. Similarly, *o*-chlorobenzaldehyde yields 1-p-*toluidino*-2-o-*chlorophenyl*-5-*methylbenziminazole,* white, monoclinic needles, m. p. 195° (*picrate,* m. p. 178—179°, *nitrosoamine,* decomp. 124°), which is reduced to *p*-toluidine and 2-o-*chlorophenyl*-5-*methylbenziminazole,* white needles, m. p. 160° (*picrate,* decomp. 189°). From *m*-nitrobenzaldehyde is similarly obtained 1-*p*-toluidino-2-*m*-nitrophenyl-5-

methylbenziminazole, greyish-yellow needles, decomp. 224—225° (*picrate*, decomp. 174°; *nitrosoamine*, decomp. 120°), and on reduction, *p*-toluidine and 2-m-*aminophenyl-5-methylbenziminazole*, white, crystalline plates, m. p. 236°. With *o*-nitrobenzaldehyde, 1-*p*-toluidino-2-*o*-nitrophenyl-5-methylbenziminazole (*picrate*, decomp. 182°; *nitrosoamine*, decomp. 130°) and 2-o-*aminophenyl-5-methylbenziminazole*, white needles, m. p. 190°; and with *p*-nitrobenzaldehyde, 1-*p*-toluidino-2-*p*-nitrophenyl-5-methylbenziminazole and 2-p-*aminophenyl-5-methylbenziminazole*, white plates, m. p. 124°, containing water of crystallisation. This base, when diazotised and coupled with β-naphthol in alcohol–pyridine solution, gives a reddish-brown azo dye, m. p. 330°. From *o*-aminoazo-*p*-toluene and *p*-dimethylaminobenzaldehyde, 1-p-*toluidino-2-dimethylaminophenyl-5-methylbenziminazole*, white needles, m. p. 249° (*picrate*, m. p. 177°; *nitrosoamine*, decomp. 85°), is obtained, which on reduction yields *p*-toluidine and the iminazole, m. p. 124°, obtained in the reduction of the base from *p*-nitrobenzaldehyde.

Benzeneazo-β-naphthylamine and benzaldehyde yield 1-anilino-2-phenylnaphthiminazole, which on reduction yields 2-phenylnaphthiminazole, m. p. 217—218°. The reduction of the condensation products of substituted benzaldehydes and benzeneazo-β-naphthylamine yields the same phenylnaphthiminazole. From *p*-hydroxybenzeneazo-β-naphthylamine (*diacetyl* derivative, m. p. 184°, *dibenzoyl* derivative, m. p. 199°) the following compounds were obtained: with benzaldehyde in alcoholic solution, 1-p-*hydroxyanilino-2-phenylnaphthiminazole*, white needles, m. p. 183° (*nitrosoamine*, decomp. 135°), which on reduction yields *p*-aminophenol and 2-phenylnaphthiminazole; with *o*-chlorobenzaldehyde, 1-p-*hydroxyanilino*-2-o-*chlorophenylnaphthiminazole*, white needles, m. p. 198° (*nitrosoamine*, decomp. 110°), and on reduction *p*-aminophenol and 2-o-*chlorophenylnaphthiminazole*, white needles, m. p. 214°; with salicylaldehyde in methyl-alcoholic solution, 1-p-*hydroxyanilino*-2-o-*hydroxyphenylnaphthiminazole*, white needles, m. p. 276°, which on reduction yields 2-o-*hydroxyphenylnaphthiminazole*, white needles, m. p. 280°; with furfuraldehyde, 1-p-*hydroxyanilino-2-furylnaphthiminazole*, white needles, m. p. 195° (*picrate*, yellow powder, *nitrosoamine*, yellow, easily decomp.). In contrast to the foregoing substituted iminazoles, which are very stable to most reducing agents, 1-p-*nitroanilino*-2-o-*chlorophenylnaphthiminazole*, bright yellow crystals, m. p. 283° (*nitrosoamine*, decomp. 105—107°), prepared from *p*-nitroanilinoazo-β-naphthylamine and *o*-chlorobenzaldehyde in acetic acid solution, yields *p*-phenylenediamine and 2-*o*-chlorophenylnaphthiminazole on reduction with zinc and acetic acid.

[With G. Seufert and H. Hojer.]—The azo dye obtained from diazotised anthranilic acid and β-naphthylamine forms crimson-red needles, m. p. 182—183°; it gives, with benzaldehyde, 1-o-*carboxyanilino-2-phenylnaphthiminazole*, colourless, monoclinic prisms, m. p. 263—264°, decomp., which on nitration in acetic acid yields 1-o-*carboxy*-p-*nitroanilino-2-phenylnaphthiminazole*, bright yellow pyramids, m. p. 274°, and this on reduction with hydriodic acid gives

2-phenylnaphthiminazole. With acetaldehyde, the same dye yields 1-o-*carboxyanilino-2-methylnaphthiminazole*, colourless, monoclinic plates, m. p. 283° (after slight decomp. at 260°), which gives 2-methylnaphthiminazole, m. p. 168° (*picrate*, m. p. 242°), on reduction.

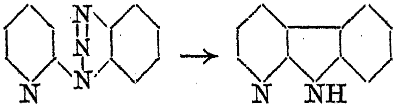
1-m-*Carboxybenzeneazo*-β-*naphthylamine*, yellowish-red needles, m. p. 220°, gives condensation products with aldehydes which are distinguished by their insolubility in solvents. The following compounds were prepared. From acetaldehyde, 1-m-*carboxyanilino*-2-*methylnaphthiminazole*, white, crystalline powder, m. p. 276°; from furfuraldehyde, 1-m-*carboxyanilino*-2-*furylnaphthiminazole*, m. p. 273—274°; from salicylaldehyde, 1-m-*carboxyanilino*-2-o-*hydroxyphenylnaphthiminazole*, colourless granules, m. p. 232° (*nitrosoamine*, decomp. 110°).

p-Carboxybenzeneazo-β-naphthylamine crystallises from benzene–alcohol in crimson-red needles, m. p. 263—264°; it condenses with aldehydes in alcoholic solution in the presence of pyridine or acetic acid. The following compounds were obtained. From benzaldehyde, 1-p-*carboxyanilino-2-phenylnaphthiminazole*, colourless prisms, m. p. 255° (decomp.) [*picrate*, m. p. 205° (decomp.), *acetyl* derivative, m. p. 218°, *nitrosoamine*, decomp. 213—214°], which on reduction yields 2-phenylnaphthiminazole and *p*-aminobenzoic acid. On nitration, the original base gives 1(2 : 4-*dinitroanilino*)-2-*phenylnaphthiminazole*, small, yellow plates, decomp. 270—272°. The dinitro compound with hydriodic acid gives 2-phenylnaphthiminazole and 1 : 2 : 4-triaminobenzene. With acetaldehyde, the azo dye gives 1-p-*carboxyanilino-2-methylnaphthiminazole*, white plates, m. p. 287° (*dinitro* derivative, m. p. 235°, yielding 2-methylnaphthiminazole on reduction). With furfuraldehyde, 1-p-*carboxyanilino*-2-*furylnaphthiminazole*, colourless prisms, m. p. 251° (greenish-yellow *nitrosoamine*).

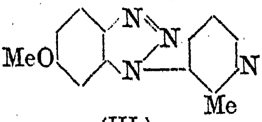
[With F. VON MANN-SIECHLER.]—The base, $C_{19}H_{16}N_4$, colourless, white plates, m. p. 228°, obtained by the action of benzaldehyde on chrysoidine (*cf.* A., 1898, i, 155) gives a *diacetyl* derivative, m. p. 105° (decomp.), a *picrate*, decomp. 204°, a *picrolonate*, decomp. 186°, and with aldehydes stable, well-crystallised benzylidene derivatives, which can be prepared directly from chrysoidine and aldehyde (2 mols.). Thus benzaldehyde and chrysoidine afford the compound $C_{26}M_{20}N_4$, bright yellow plates, m. p. 242° (*nitrosoamine*, decomp. 110°), which with 10% sulphuric acid affords benzaldehyde and 1-anilino-2-phenylaminobenziminazole, white flocks, m. p. 229°. Similarly, chrysoidine and salicylaldehyde give the compound $C_{26}H_{20}O_2N_4$, bright yellow plates, m. p. 242° (*nitrosoamine*, decomp. 125°), from which dilute sulphuric acid splits off 1 mol. of salicylaldehyde. By diazotisation in alcoholic solution and treatment with 95% alcohol, the base $C_{19}H_{16}N_4$ was converted into 1-*anilino*-2-*phenylbenziminazole*, snow-white prisms, m. p. 211° (*picrate*, decomp. 199°; *picronolate*, decomp. 220°; *nitrosoamine*, decomp. 137°), and this on reduction with hydriodic acid gives the known 2-phenylbenziminazole.

[With F. ELFLEIN and K. MÜLLER.]—The action of benzyl chloride on benzeneazo-β-naphthylamine, either alone or in acetic acid solution, gives aniline and 2-phenylnaphthiminazole. Similar results were obtained with *p*-tolueneazo-β-naphthylamine, *o*- and *m*-nitrobenzeneazo-β-naphthylamine, and *p*-anisoleazo-β-naphthylamine. Similarly, benzeneazo-β-benzylnaphthylamine (shining, light red needles, m. p. 136—138°), obtained by coupling benzyl-β-naphthylamine with benzene diazonium chloride in alcoholic solution, on boiling with alcoholic hydrochloric acid decomposes into aniline and 2-phenylnaphthiminazole. Similar results were obtained with *p*-tolueneazo-benzyl-β-naphthylamine and nitrobenzeneazobenzyl-β-naphthylamine. R. B.

Harmine and Harmaline. VII. Synthesis of *apo*Harmine and of certain Carboline and Copyrine Derivatives. W. Lawson, W. H. Perkin, jun., and R. Robinson (*J. Chem. Soc.*, 1924, **125**, 626—657).—2-Chloropyridine and *o*-phenylenediamine condense to give *o*-aminophenyl-2-pyridylamine hydrochloride,



(I.) (II.)

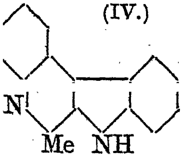


(III.)

which, when treated with nitrous acid, yields 1-α-*pyridylbenzotriazole* (I), colourless needles, m. p. 110—111°. The latter, when heated in small quantities with zinc chloride, gives 3-*carboline* (II), colourless needles, m. p. 210°; *hydrochloride*, needles from dilute hydrochloric acid; *mercurichloride*, needles; *hydrogen oxalate*, needles from dilute oxalic acid solution; *picrate*, canary-yellow needles, m. p. 260—264°. 2-Chloroquinoline and *o*-phenylenediamine similarly give 1-α-*quinolylbenzotriazole*, colourless prisms or needles, m. p. 145°, which, when heated, gives quinindoline, identical with that of Gabriél and Eschenbach (A., 1898, i, 199). The triazole (III) cannot be prepared by this method owing to the inactivity of β-halogen substituents in the pyridine molecule, and alternatively the preparation of 3-aminoquinaldine and 3-amino-2-methylpyridine was undertaken for condensation with the requisite halogen derivatives. 2-Methylquinoline-3 : 4-dicarboxylic acid (cf. Pfitzinger, A., 1898, i, 207), when strongly heated, gives the *anhydride*, colourless prisms, m. p. 218°, and when heated with carbamide at 230° gives the *imide*, pale yellow needles from ethyl acetate, m. p. 257°. The imide, when treated with bromine and potassium hydroxide, gives 3-*amino*-2-*methylquinoline*-4-*carboxylic acid*, pale yellow needles, m. p. 221—222° (decomp.), which, when heated at 225°, is smoothly converted into 3-amino-2-methylquinoline, m. p. 160—160·5°, identical with that prepared by Stark (A., 1907, i, 973). The condensation of this aminoquinaldine with various chlorobenzene derivatives could not be carried out, and is still under investigation.

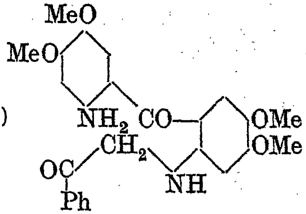
Ethyl β-aminocrotonate and ethyl cinnamoylpyruvate condense to give *ethyl styrylmethylpyridinedicarboxylate*, which is isolated as a picrate, yellow needles, m. p. 147·5—148°. These, on treatment with ammonia and subsequent hydrolysis, give *styrylmethylpyridine*-

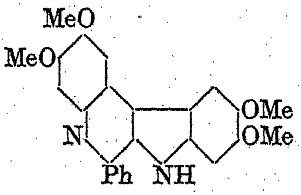
dicarboxylic acid, pale yellow prisms, m. p. 220—221°. This acid cannot be 4-styryl-2-methylpyridine-3 : 6-dicarboxylic acid, since, when boiled with aniline, it gives a *phenylimide*, which was isolated in two forms, (*a*), bright yellow needles, m. p. 228—230°, (*b*), yellow needles, m. p. 203—204°; *a* and *b* may be geometrical stereoisomerides, although *a* on recrystallisation from xylene gave *b*. The potassium salt of the dicarboxylic acid, on treatment with potassium permanganate, gives 2-*methylpyridine*-3 : 4 : 6-*tricarboxylic acid*, which was isolated as the *potassium barium* salt, colourless crystals, and also gives a *monopotassium* salt, colourless prisms, a characteristic *ferrous* salt, red or orange-brown prisms, and on treatment with an excess of aniline gives the *anilide phenylimide*, pale yellow needles, m. p. 237°, and also the *phenylimide* of 2-methylpyridine-3 : 4-dicarboxylic acid, colourless plates, m. p. 190°. The *tricarboxylic acid* itself crystallises from water in prisms $+3H_2O$, which, when anhydrous, darken at 219° and melt at 223° (decomp.), and was found not to be identical with the methylpyridinetricarboxylic acid obtained by Dobbie and Lauder (T., 1902, **81**, 154) from corydaline, the constitution of which is therefore still in doubt. The tricarboxylic acid in turn gives 2-methylpyridine-3 : 4-dicarboxylic acid, m. p. 252—256°. The synthesis of a substituted dibenzo*apo*harmine of the type (IV) was then undertaken in order that subsequent oxidation of the benzene nuclei should furnish *apo*harmine. Veratrone, the preparation of which from veratric acid has been greatly improved, was converted by nitric acid into 6 : 6′-*dinitro*-3 : 4 : 3′ : 4′-*tetramethoxybenzophenone* (dinitroveratrone), colourless needles from acetic acid, m. p. 225°, and the latter on reduction gives *diaminoveratrone*, yellow prisms, m. p. 210°. The 6 : 6′-position of the nitroxyl groups in dinitroveratrone is confirmed by converting diaminoveratrone into *diacetyldiaminoveratrone*, pale yellow needles, m. p. 203°, which, on treatment with nitric acid in acetic acid suspension, gives a theoretical yield of 6-nitroacetoveratrylamine (cf. Jones and Robinson, T., 1917, **111**, 914).



(IV.)

Diaminoveratrone, when heated with ω-bromoacetophenone in acetic acid, gives the hydrobromide of N-*phenacyldiaminoveratrone*, the *base* itself (V) forming greenish-yellow needles, m. p. 185—186° (decomp.). The base, when treated in alcoholic suspension with 30% aqueous potassium hydroxide, gives *phenyldiveratroharmyrine* (phenyldiveratro-7-pyridole) (VI), which crystallises from methyl alcohol +1 mol. of solvent, prisms, m. p. 145—148° (decomp.).

(V.)


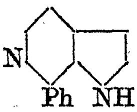


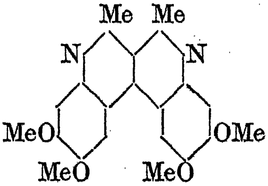
(VI.)

Replacement of the ω-bromoacetophenone by bromoacetone gave no compound analogous to *N*-phenacyldiaminoveratrone, but *methyldiveratroharmyrine* was obtained, colourless prisms, m. p. 254°, and gave a *methosulphate*, orange-yellow needles. The hydrobromide, on boiling with hydriodic acid, was completely demethylated, giving *methyltetrahydroxydibenzoharmyrine hydriodide*, yellow needles. Methyl- and phenyl-diveratroharmyrine were found on oxidation and subsequent treatment with alkali to give, however, only a minute yield of the corresponding *apo*harmine (VII), owing to almost complete destruction of the base by the oxidising agent.

2 : 7-Naphthyridine (copyrine) rings may be synthesised also from the 2 : 2-diaminobenzophenones. Thus diaminoveratrone condenses with acetylacetone to give *dimethyldiveratrocopyrine* (VIII), colourless needles from *n*-butyl alcohol, m. p. 230—231°, forming a yellow, crystalline *nitrate*, and a *picrate* of composition $3C_{22}N_{22}O_4N_2\cdot5C_6H_3O_7N_3$, yellow needles, decomp. 245°. Diaminoveratrone with benzoylacetone gives similarly *phenylmethyldiveratrocopyrine*, colourless needles, m. p. 270°; with dibenzoylmethane gives *diphenyldiveratrocopyrine*, yellow needles, m. p. 362°, and with 1 : 3-diketohydrindene gives o-*phenylenediveratrocopyrine*, isolated as the *acetate*, yellow needles, the latter being converted by ammonia into the *base*, yellow needles, from nitrobenzene–*n*-butyl alcohol, m. p. 304°. Diaminoveratrone condenses also with ethyl acetoacetate to give *hydroxymethyldiveratrocopyrine*, pale yellow needles from quinoline, m. p. 320—330°; with ethyl malonate to give *dihydroxydiveratrocopyrine*, yellow needles from nitrobenzene, m. p. 300° (decomp.); with ethyl cyanoacetate to give *aminohydroxydiveratrocopyrine*, salmon-coloured needles from alcohol–nitrobenzene, decomp. 280°, chars 280—290°.

(VII.)

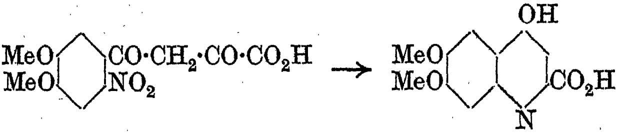




(VIII.)

Xanthone (*oo*′-dichlorobenzophenone) can be prepared by the dry distillation of calcium *o*-chlorobenzoate. A mixture of ethyl benzoylacetate and ethyl β-aminocrotonate, when boiled in methyl-alcoholic potassium hydroxide, yields 6-hydroxy-4-phenyl-2-methylpyridine-3-carboxylic acid (cf. Ruhemann, T., 1899, **75**, 412).

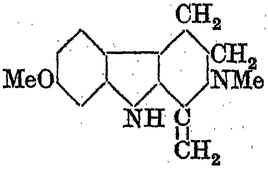
The following synthesis of a dimethoxykynurenic acid has been accomplished. Acetoveratrone on nitration does not yield 4 : 5-dinitroveratrole (Harding, T., 1914, **105**, 2795), but 6-*nitroacetoveratrone*, pale yellow needles, m. p. 133—133·5°, in which the 6-position of the nitro group is shown by further nitration, giving 4 : 5-dinitroveratrole. 6-*Nitroacetoveratrone* condenses with anisaldehyde to give 6-*nitro*-3 : 4-*dimethoxyphenyl* 4-*methoxystyryl ketone*, pale-yellow prisms from ethyl acetate, m. p. 170°, and also gives a *piperonylidene* derivative, plates and needles, m. p. 176—177°, re-solidify and then re-melt above 200° (indef.). The 6-nitro compound on reduction gives 6-*aminoacetoveratrone*, colourless prisms, m. p. 133°, and when treated with sodium ethoxide and ethyl oxalate in alcohol yields 6-*nitroveratroylpyruvic acid* (IX), needles, m. p. 163°. The latter, when reduced with ferrous hydroxide,

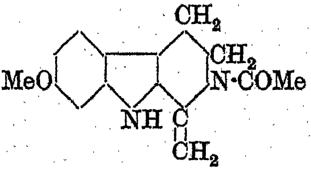
(IX.)  (X.)

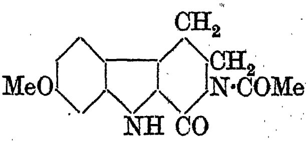
gives 4-*hydroxy*-6 : 7-*dimethoxyquinoline*-2-*carboxylic acid* (dimethoxykynurenic acid) (X), needles, sintering at 260°, m. p. 270° (decomp.). This acid when heated in glycerol solution loses carbon dioxide, giving 4-*hydroxy*-6 : 7-*dimethoxyquinoline*, colourless prisms, softening at 165—170°, re-solidifying and melting at 226°.

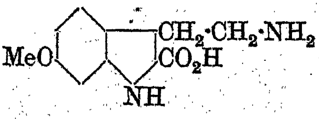
5 : 7-Dibromoisatin was converted into 5 : 7-dibromoisatinic acid, and the latter into 6 : 8-*dibromo*-2-*methylquinoline*-4-*carboxylic acid*, colourless needles, m. p. 267° (decomp.). The latter on heating gives 6 : 8-*dibromo*-2-*methylquinoline*, needles, m. p. 100°, *picrate*, orange-yellow needles, m. p. 155°. Attempts made to replace the bromine in the carboxylic acid by hydroxy groups and then by oxidation of the benzene nucleus to obtain 2-methylpyridine-4 : 5 : 6-tricarboxylic acid failed. F. G. M.

Harmine and Harmaline. VIII. Constitution of certain Harmaline Derivatives. H. Nishikawa, W. H. Perkin, jun., and R. Robinson (*J. Chem. Soc.*, 1924, **125**, 657—663).—Methylharmaline on oxidation with potassium permanganate in acetone solution yields keto*iso*normethyltetrahydroharmine; acetylharmaline when thus oxidised yields *acetylketotetrahydronorharmine* (III), colourless prisms, m. p. 207—208°, and when reduced with hydrogen in the presence of palladium gives acetyltetrahydroharmaline.

(I.) 

 (II.)

(III.) 

 (IV.)

It follows that methyl- and acetyl-harmaline have the constitution (I) and (II). Harmaline methosulphate on treatment with potassium cyanide gives *cyanomethyltetrahydroharmine*, colourless leaflets, m. p. 155—156°, whilst harmine methosulphate gives a similar but unstable product, m. p. 141°. Acetylketotetrahydronorharmine on hydrolysis with alcoholic potassium hydroxide yields *6-methoxy-3-β-aminoethylindole-2-carboxylic acid* (IV), leaflets, decomp. 220—250°, and the corresponding *lactam, ketotetrahydronorharmine*, prisms, m. p. 198°. The lactam could not be hydrolysed to the amino-acid, or the latter dehydrated to the lactam. Hydratoacetylharmaline, which forms a *hydrochloride* (+0·5 aq.), colourless needles, on acetylation gives two isomeric *diacetylhydratoacetylharmalines*, (*a*) needles, m. p. 134—135°, (*b*) pale-yellow plates, m. p. 159—160°. The work of O. Fischer (A., 1898, i, 164; 1914, i, 316) is thus confirmed. F. G. M.

Dyes Derived from Phenanthraquinone. IV. Anilinoflavindulines and Phenanthraquinoneazo-dyes. A. C. Sircar and D. C. Roy (*J. Chem. Soc.*, 1924, **125**, 543—547; cf. T., 1913, **103**, 295; 1921, **119**, 1211; 1922, **121**, 1944).—The following phenanthraphenazonium compounds containing an anilino group attached to the benzenoid nucleus did not exhibit the expected property of dyeing in blue shades.

4 : 5-*Dibromo*-11-*anilinoflavinduline chloride*, prepared by reducing nitrosodiphenyl-*m*-phenylenediamine and condensing the product with 4 : 5-dibromophenanthraquinone, green crystals, decomp. 199°, m. p. 245—252°. 2 : 7-*Dinitro*-11-*anilinoflavinduline chloride*, similarly prepared (not crystalline), blackens at 250°, m. p. above 270°. 2-*Nitro*-11-*anilinoflavinduline chloride*, prisms, m. p. above 270°. 2 : 7-*Diamino*-11-*anilinoflavinduline chloride*, bluish-black flocculent precipitate, m. p. above 275°. 4 : 5 : 11-*Trianilinoflavinduline chloride*, prepared from the above 4 : 5-dibromo compound by the action of aniline in the presence of copper powder, is a flocculent precipitate, decomp. 165°, m. p. 205—210°.

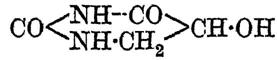
The following azo compounds were prepared by coupling the diazotised aminophenanthraquinone with the hydroxy acid in alkaline solution. 1-Hydroxy-2-naphthoic acid with 2-aminophenanthraquinone gives 4-*hydroxy*-1(2′)-*phenanthraquinoneazo*-3-*naphthoic acid*, m. p. not below 275°; with 4-aminophenanthraquinone gives 4-*hydroxy*-1(4′)-*phenanthraquinoneazo*-3-*naphthoic acid*; with 2 : 7-diaminophenanthraquinone gives *phenanthraquinone*-2 : 7-*bis*(1-*azo*-4-*hydroxy*-3-*naphthoic acid*), m. p. not below 283°; with 4 : 5-diaminophenanthraquinone gives *phenanthraquinone*-4 : 5-*bis*(1-*azo*-4-*hydroxy*-3-*naphthoic acid*), amorphous, m. p. above 275°.

2-Hydroxy-3-naphthoic acid with 2-aminophenanthraquinone gives 2-*hydroxy*-1(2′)-*phenanthraquinoneazo*-3-*naphthoic acid*, blue crystals, decomp. 225°; with 4-aminophenanthraquinone gives 2-*hydroxy*-1(4′)-*phenanthraquinoneazo*-3-*naphthoic acid*, decomp. 250—255°; with 2 : 7-diaminophenanthraquinone gives *phenanthraquinone*-2 : 7-*bis*(1-*azo*-2-*hydroxy*-3-*naphthoic acid*), crystals, m. p. not below 283°; with 4 : 5-diaminophenanthraquinone gives *phenanthraquinone*-4 : 5-*bis*(1-*azo*-2-*hydroxy*-3-*naphthoic acid*), m. p. not below 274°. Salicylic acid gives with 4-aminophenanthraquinone *phenanthraquinone-4-azosalicylic acid*, m. p. not below 275°; with 2 : 7-diaminophenanthraquinone gives *phenanthraquinone-2 : 7-bis-azosalicylic acid*, m. p. not below 270°; with 4 : 5-diaminophenanthraquinone gives *phenanthraquinone-4 : 5-bisazosalicylic acid*, m. p. not below 274°. The dyeing properties on wool of the above compounds and the colours developed in sulphuric acid solution are described. F. G. M.

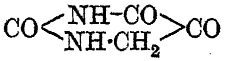
Reaction of Azine and Thiazine Dyes with the Gel of *Chondrus crispus*. E. JUSTIN-MUELLER (*Bull. Soc. chim.*, 1924, **35**, 390—394).—Azine and thiazine dyes coagulate solutions of the gel obtained from lichen carragheen, *Chondrus crispus*. This property is not possessed by the oxazines, and appears to be characteristic of the "az-azonium" and "az-thionium" groupings. R. B.

Catalysis. IV. Behaviour of the Amino Group when Cytosine and Nitrouracil are reduced in the Presence of Colloidal Platinum. E. B. BROWN and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1924, **46**, 702—708).—Cytosine is reduced by hydrogen in the presence of colloidal platinum with formation of hydrouracil and ammonia. Partial reduction of 5-nitrouracil with three molecular equivalents of hydrogen forms 5-aminouracil, which compound undergoes partial hydrolysis with the production of 5-hydroxyuracil (*iso*barbituric acid); with four molecular equivalents of hydrogen the hydrolysis proceeds further and a new *compound* (I) or (II) (?) is obtained. It forms diamond-shaped crystals not melting at 285°. Yeast-nucleic acid was also submitted to the action of hydrogen in presence of colloidal platinum, and evidence of the formation of ammonia obtained. C. J. S.

(I.)



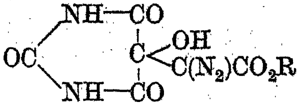
$CO<\begin{matrix}NH-CO\\NH\cdot CH_2\end{matrix}>CH\cdot OH$



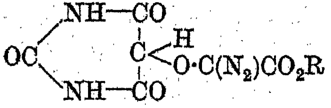
$CO<\begin{matrix}NH-CO\\NH\cdot CH_2\end{matrix}>CO$

(II.)

Interaction of Ethyl Diazoacetate and Alloxan. H. BILTZ and E. KREMER (*Annalen*, 1924, **436**, 154—173).—Ethyl diazoacetate combines with alloxan to give ethyl dialuryldiazoacetate (I) or (II).



(I.)



(II.)

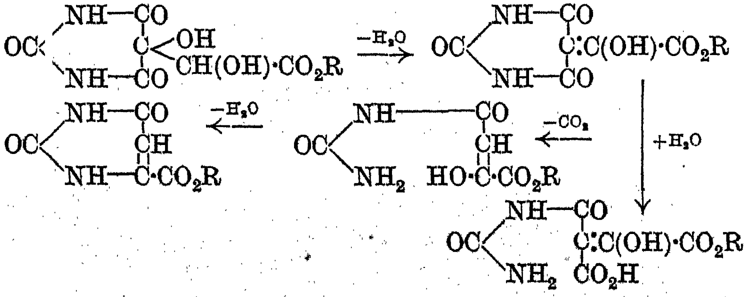
Formula I best explains the results of methylation (to give trimethyl derivative) and the decomposition effected by alkalis, acids, and oxidising agents. Formula II is also possible, since the ester cannot be acetylated, and since among its reduction products are formed dialuric acid and alloxantin.

Ethyl dialuryldiazoacetate is produced by the interaction of alloxan hydrate (1 mol.) and ethyl diazoacetate (2·5 mols.), when yellow, six-sided plates, decomp. 163—164°, are obtained. The *disodium* salt, $C_8H_6O_6N_4Na_2$, is described. Nitrogen is evolved when the ester is treated with dilute mineral acids or Fehling's solution. *Methyl dialuryldiazoacetate* (from alloxan hydrate and methyl diazoacetate), forms six-sided, yellow needles, decomp. 153—154°.

Ethyl methyl dialuryldiazoacetate (from methylalloxan hydrate) forms prisms, decomp. 136°. Methylalloxan will not give a solid derivative with methyl diazoacetate, whilst dimethylalloxan will not react with either ester.

Methyl 1 : 3 : 5-*trimethyldialuryldiazoacetate* is produced when ethyl dialuryldiazoacetate and diazomethane react in ethereal solution. It forms clusters of prisms, m. p. 99—100°, and when warmed with dilute sulphuric acid affords two atoms of nitrogen. When oxidised with concentrated nitric acid, dimethylalloxan anhydride and oxalic acid are produced; with hydroxylamine, it gives dimethylvioluric acid.

Ethyl dialuryldiazoacetate, on warming with *N*/2-sodium hydroxide, evolves nitrogen, and on acidification, ethyl uracilcarboxylate and carbon dioxide are produced. Uracilcarboxylic acid is also formed in the above reactions, as microscopic needles, m. p. not below 330°, and was characterised as the 5-nitro derivative. The formation of these compounds must take place according to the scheme :



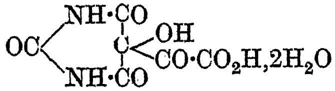
Ethyl dialuryldiazoacetate on hydrolysis with dilute hydrochloric acid yields ethyl glycollate and alloxantin; with concentrated hydrochloric acid, it yields dialuric acid and ethyl glyoxylate.

Another product with either dilute or concentrated hydrochloric acid is ethyl uracilcarboxylate. The methyl ester yields *methyl uracilcarboxylate* (fine needles, m. p. 230°) on hydrolysis with the concentrated acid.

Ethyl 5-ethoxyuracil-6-carboxylate results from the interaction of dialuryldiazoacetate and alcoholic hydrogen chloride, when nitrogen is evolved, and the ester may be obtained as long, colourless needles, m. p. 203—212°. The *ammonium* salt (pale, rose-coloured plates, m. p. 202—203°) and the *potassium* salt (colourless) are described, and from the latter the free *acid* may be obtained by the action of concentrated hydrochloric acid. It forms colourless prisms, decomposing at 216—217° or on heating at 190°, to give ethyl *iso*barbiturate.

Oxidation of ethyl 5-ethoxyuracil-6-carboxylate with permanganate yields oxaluric and oxalic acids.

Oxidation of ethyl dialuryldiazoacetate with concentrated nitric acid gives alloxan and oxalic acid, and with milder conditions *dialurylglyoxylic acid* dihydrate [microscopic needles, m. p. 152° (decomp.)] may be isolated (annexed formula). With hydrogen peroxide, oxaluric acid is formed.



$$OC<\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}>C<\begin{matrix}OH\\ CO\cdot CO_2H,2H_2O\end{matrix}$$

Reduction of ethyl dialuryldiazoacetate with hydriodic acid gives alloxantin and ethyl iodoacetate, whereas with stannous chloride, the products are dialuric and glycollic acids. A. E. C.

Oxidation of Uric Acid. H. Biltz and H. Schauder (*J. pr. Chem.*, 1923, [ii], **106**, 108—172).—The oxidation of uric acid in dilute acetic acid suspension at 0°, using potassium permanganate (2·6 atoms of oxygen), affords potassium oxalurate and oxalate, carbamide, and oxalyldiureide; when the permanganate used affords 1 atom of oxygen, the same products except the oxalurate are obtained. Oxidation of uric acid with potassium persulphate in presence of potassium acetate is less vigorous than the above and requires water-bath temperatures; when persulphate equivalent to 1 atom of oxygen is used, allantoin results, 2 atoms of oxygen affording potassium oxalurate and oxalyldiureide. Oxidation of uric acid at 0° in aqueous suspension using permanganate (=2 atoms O) in presence of a rapid current of carbon dioxide gives the products obtained by using acetic acid, whilst with permanganate equivalent to 1 atom of oxygen, potassium oxalurate and oxalate and carbamide result. No uroxanic acid is isolated, probably because its precursor, the hypothetical hydroxyacetylenediureinecarboxylic acid, loses carbon dioxide before passing into uroxanic acid.

When uric acid is boiled with aqueous hydrogen peroxide until it is all dissolved, carbonyl dicarbamide is the main product, and is accompanied by a trace of cyanuric acid and a *substance* forming white, hemispherical masses, decomp. 220°. The results are unaffected by adding small quantities of acetic acid or of potassium acetate.

Oxidation of uric acid by permanganate (=1 atom O) at the ordinary temperature in presence of sulphuric acid gives alloxan and alloxantin, whilst if the acid is boiled with aqueous potassium persulphate solution (=1 atom O) alloxan is formed in small quantities, the majority of the acid probably passing into alloxanic acid and the latter into 5-hydroxyhydantoin (A., 1921, i, 815). When twice the above proportion of persulphate is used, a little parabanic acid is formed, presumably from alloxan.

Hydrogen peroxide converts uric acid in presence of boiling dilute sulphuric acid into parabanic acid (formed from alloxan). In presence of boiling dilute hydrochloric acid, the oxidation is so satisfactory that the author recommends this as a method of preparing parabanic acid.

Possible intermediate compounds in the oxidation of uric to oxaluric acid are uric acid glycol, alloxan, allantoin, or the hypothetical hydroxyacetylenediureinecarboxylic acid. These compounds require for their formation (from uric acid) 1 atom of oxygen, this amount of oxygen being required to convert them into oxaluric acid. The compounds have therefore been oxidised under different conditions. Uric acid 4 : 5-glycol, when treated with permanganate (=1 atom O) in dilute acetic acid at 0°, is very slowly oxidised and affords impure potassium oxalurate and oxalate. In boiling solution, oxidation is rapid, but the yield of oxalurate is small. The glycol is therefore not the intermediate between uric and oxaluric acids.

9-Methyluric acid 4 : 5-glycol, oxidised with permanganate and acetic acid in the warm, gives methyloxaluric acid (?), m. p. 180—190° (with frothing). 7 : 9-Dimethyluric acid 4 : 5-glycol similarly affords small quantities of dimethylparabanic acid.

Alloxan is very slowly oxidised by cold permanganate and dilute acetic acid to give potassium oxalurate. Oxidation is more rapid in the warm, but alloxan is clearly not the intermediate sought for. Hydrogen peroxide oxidises alloxan at water-bath temperatures to give oxaluric acid.

Allantoin is slowly oxidised by cold and rapidly by warm permanganate, potassium oxalurate and carbamide resulting. Allantoin is ruled out as the intermediate oxidation product, which is evidently the hypothetical hydroxyacetylenediureinecarboxylic acid.

A method is given for the preparation of potassium oxalurate from uric acid and consists in the oxidation of the latter in alkaline solution, and then in acetic acid solution, using permanganate equivalent to one atom of oxygen for each stage. Potassium oxalurate ($C_3H_3O_4N_2K,H_2O$), when treated with hydrochloric acid, affords *oxaluric acid*, decomp. 208—210°. The *ammonium* salt is described. *Methyl oxalurate*, from the acid and diazomethane, forms crystals, m. p. 192° (indef. with frothing). *Oxaluric methylamide*, from the ester and aqueous methylamine, forms needles, decomp. 251—253°. When oxaluric acid is boiled for a short time with water, carbamide oxalate and ammonium tetraoxalate result. The monocarbamide oxalate described by Lubavin (1872) does not exist. If equimolecular quantities of carbamide and oxalic acid are mixed in aqueous solution, carbamide oxalate, $H_2C_2O_4,2CO(NH_2)_2$, separates, whilst if the solution is boiled for some time, ammonium oxalate is formed.

When 1 : 3-dimethyluric acid is oxidised with alkaline permanganate (=1 atom O), potassium oxalurate and *s*-dimethyloxamide result. Alkaline oxidation (1 atom O) followed by acid oxidation (acetic; 1 atom O) affords potassium oxalurate and dimethylparabanate, together with *s*-dimethyloxamide and oxaluric methylamide. Oxidation (1 atom O) in acetic acid solution gives dimethylparabanic acid and a crystalline *substance* (not examined), oxidation with 2 atoms of oxygen (as permanganate) affording potassium oxalurate and dimethylparabanic acid. Oxidation of 1 : 3-dimethyluric acid with alkaline hydrogen peroxide affords a *substance* forming needles, m. p. 215° (decomp.).

3 : 7-Dimethyluric acid when oxidised by alkaline permanganate (1 atom O) gives 1 : 8-dimethylallantoin together with a *potassium* salt, $C_6H_4O_5N_3K$, plates, m. p. 275° (indef. and decomp.) (corresponding with an *acid*, $C_6H_5O_5N_3$, prisms, decomp. 212°). 3 : 7-Dimethyluric acid is converted by alkaline hydrogen peroxide into carbonyl dicarbamide (?), decomp. 210°.

No alloxan is formed when chlorine is passed into a suspension of uric acid in aqueous sodium acetate–acetic acid. No alloxans are formed when 9-methyluric acid glycol is heated with hydrochloric acid, the products being carbamide and methylparabanic acid. Similarly treated, 7 : 9-dimethyluric acid glycol affords carbamide and dimethylparabanic acid. The glycol type is therefore not intermediately formed when uric acids are oxidised to alloxans.

5-Chloro- and 5-hydroxy-ψ-uric acids are readily converted by hydrochloric acid into alloxan, which is conveniently identified by adding stannous chloride and isolating alloxantin.

The chloraluric acid described by Schiel (1859) is, as stated by Lubavin (*loc. cit.*), a mixture of ammonium chloride and parabanic acid. The stryphnic acid obtained by Gibbs (1869) on treating uric acid with potassium nitrite and mineral acid, is now shown to be a mixture of allantoin with oxaluric and oxalic acids. Similarly, the urinilic acid described by Sokolov (1869) does not exist; nitric oxide has no action on an aqueous suspension of uric acid, whilst nitrogen peroxide has no action on uric acid in absence of water; nitric oxide containing a little nitrogen peroxide converts uric acid, in aqueous suspension, into uric acid glycol, parabanic acid, and alloxan, whilst nitric oxide containing much nitrogen peroxide affords xanthine, parabanic acid, alloxan, and oxalic acid.

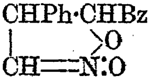
The paper contains a useful discussion of the results obtained.

E. E. T.

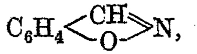
Potassium Hydroxyhæmin. A. Hamsik (*Z. physiol. Chem.*, 1924, **133**, 173—179).—The author has previously (*Spisy lékařské fakulty v Brně*, 1922, **1**, 1A, 5), by extracting the coagulum of blood with alcohol acidified with oxalic acid, obtained a compound $C_{34}H_{31}O_4N_4Fe$, small star-like aggregates of crystals, which he named hydroxyhæmin anhydride. By boiling the anhydride with glacial acetic acid and sodium chloride or with alcohol, oxalic acid, and sodium chloride, α-chlorohæmin was obtained. Potassium hydroxyhæmin, $C_{34}H_{30}O_4N_4K_2Fe\cdot OH$, very small spherical, crystalline aggregates, was obtained by treating hydroxyhæmin anhydride or α-chlorohæmin with alcoholic potassium hydroxide.

S. S. Z.

A New Type of Cyclic Compound. E. P. Kohler (*J. Amer. Chem. Soc.*, 1924, **46**, 503—517; cf. A., 1916, i, 404; 1919, i, 582).—Improved methods are described for the preparation of phenyl γ-nitro-β-phenylpropyl ketone and of its α-bromo derivative, which occurs in two stereoisomeric forms, needles, m. p. 108°, and plates or prisms, m. p. 129°, and is accompanied, in its formation, by the *αα-dibromo* derivative, tablets, m. p. 106°. The α-bromo derivative, when treated with potassium acetate in methyl-alcoholic solution, affords a mixture of the *cyclo*propane derivative previously described with *2-hydroxy-3-methoxy-5-benzoyl-4-phenylisoxazolidine* and an unidentified oxazole (?) derivative. If the isoxazolidine (prisms, m. p. 162°) is dissolved in glacial acetic acid and the solution poured into water, *2 : 3-dihydroxy-5-benzoyl-4-phenylisoxazolidine*, prisms, m. p. 153°, results (*dibenzoyl* derivative, tablets, m. p. 158—160°). The isoxazolidine (m. p. 162°), when treated with ammonia, affords *3-amino-2-hydroxy-5-benzoyl-4-phenylisoxazolidine*, needles, m. p. about 162° (decomp.); this substance, when boiled with ethyl alcohol in presence of acetic acid, being converted into *2-hydroxy-3-ethoxy-5-benzoyl-4-phenylisoxazolidine*, m. p. 168° (decomp.), boiling with methyl alcohol etc. affording the above methoxy compound. The latter, when treated with acetic anhydride, is slowly converted into *phenyl γ-nitro-α-acetoxy-β-phenylpropyl ketone* (tablets, m. p. 98°), which with ammonia affords the corresponding *α-hydroxy* compound (m. p. 142°; *benzoyl* derivative, needles, m. p. 106—107°). The last-named hydroxy compound, when treated with hydrogen chloride in methyl-alcoholic solution, is converted into the methoxyisoxazolidine of m. p. 162°. The formation from the latter of the above ketone (m. p. 98°) takes place through the intermediate production of *5-benzoyl-4-phenylisoxazoline oxide*, colourless tablets, m. p. 126° (annexed formula). This compound, which results when the above α-bromoketone is treated with potassium acetate in *iso*propyl-alcoholic solution, combines with water, and with primary (but not with secondary) alcohols, in presence of acid, to give isoxazolidines, water, *e.g.*, affording the dihydroxyisoxazolidine mentioned above, whilst ammonia affords the above aminohydroxyisoxazolidine. The isoxazolidines described form sparingly soluble copper salts. The methoxyisoxazolidine, which is converted at its m. p. into methyl alcohol, water, benzonitrile, and a nitrogenous substance, affords a *benzoyl* derivative (colourless plates, m. p. 114°) and a *copper* derivative, $C_{17}H_{17}O_5NCu$, and (like the isoxazoline oxide) is converted by alkali into benzonitrile, and formic and phenylacetic acids.



A. B. S.

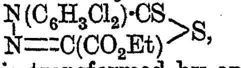
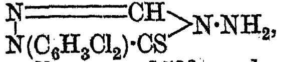
Indoxazens and *iso*Oxazoles. K. VON AUWERS (*Ber.*, 1924, 57, [*B*], 461—467).—A comparison of the optical properties of indoxazen with those of *iso*oxazole and its derivatives confirms the structure,  $C_6H_4<\overset{CH}{\underset{O}{>}}N$, ascribed to the former compound by Conduché (A., 1908, i, 154). The following data, amongst others, are recorded. *iso*Oxazole, b. p. 95°, d_4^{20} 1·078, n_{He}^{20} 1·428. 5-Methyl-*iso*oxazole, b. p. 122°, d_4^{20} 1·023, n_{He}^{20} 1·439. 3-Methyl*iso*oxazole, b. p. 118°, d_4^{20} 1·022, n_{He}^{20} 1·435. 3 : 5-Dimethyl*iso*oxazole, b. p. 143°, d_4^{20} 0·983, n_{He}^{20} 1·442. 3 : 4 : 5-Trimethyl*iso*oxazole, b. p. 111°/75 mm., d_4^{20} 0·981, n_{He}^{20} 1·452. 3 : 4-Tetramethylene*iso*oxazole,

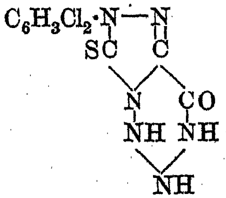
$C_6H_8\lessdot\begin{matrix}CH\\N\!-\!-\end{matrix}\!>\!O$, b. p. 93°/15 mm., d_4^{20} 1·095, n_{He}^{20} 1·498. Methyltetrahydrobenzo-3 : 4-*iso*oxazole, b. p. 97°/16 mm., d_4^{20} 1·059, n_{He}^{20} 1·491. Methyltetrahydrobenzo-4 : 5-*iso*oxazole, b. p. 101°/18 mm., d_4^{20} 1·062, n_{He}^{20} 1·492.

Indoxazen, b. p. 84°/11 mm., d_4^{20} 1·170, n_{He}^{20} 1·563. 3-Phenylindoxazen, $C_6H_4<\begin{matrix}CPh\\-O-\end{matrix}\!\gtrdot N$, m. p. 83—84°, b. p. 181°/13 mm., $d_4^{39\cdot9}$ 1·1241, $n_{He}^{39\cdot9}$ 1·59279. Salicylonitrile, $d_4^{99\cdot6}$ 1·1052, $n_{He}^{99\cdot6}$ 1·54359. *o*-Methoxybenzonitrile, b. p. 146°/20 mm., d_4^{20} 1·107, n_{He}^{20} 1·548. *o*-Anisaldoxime methyl ether, b. p. 235°, d_4^{20} 1·092, n_{He}^{20} 1·554.

Attempts to convert *o*-aminoacetophenone into 3-methylindoxazen gave unexpectedly methylanthranil, $C_6H_4\lessdot\begin{matrix}CMe\\N\!-\!-\end{matrix}\!>\!O$, b. p. 121°/17 mm., $d_4^{23\cdot2}$ 1·1304, $n_{He}^{23\cdot2}$ 1·57457. H. W.

Synthesis of Thiobiazolone Derivatives. C. Bülow and F. Seidel (*Ber.*, 1924, **57**, [*B*], 357—362).—Thiobiazolone sulphides may be obtained simply by the action of potassium xanthate on the 2 : 4-dichlorophenylhydrazone of ethyl α-chloroglyoxylate and analogous substances (cf. Bülow and Neber, A., 1913, i, 207, 999; 1916, i, 845).

The 2 : 4-dichlorophenylhydrazone of ethyl α-chloroglyoxylate, $C_6H_3Cl_2\cdot NH\cdot N{:}CCl\cdot CO_2Et$, is converted by potassium xanthate in warm alcoholic solution into *ethyl* 5-*thio*-4-op-*dichlorophenylthiobiazolone-2-carboxylate*,  $\left.\begin{matrix}N(C_6H_3Cl_2)\cdot CS\\ N{=}C(CO_2Et)\end{matrix}\right>S$, small, colourless needles, m. p. 122°, which is transformed by an alcoholic solution of ammonia into the corresponding *amide*, $C_9H_5ON_3S_2Cl_2$, colourless needles, m. p. 235°; the hydrolysis of the ester or amide to the acid could not be effected. A *substance*, $C_{21}H_{16}O_4N_4Cl_4S_2$, m. p. 158—160° or 173° (when crystallised from alcohol or acetic acid, respectively) is obtained as by-product of the preparation of the ester. The latter compound is converted by prolonged treatment with an excess of hydrazine hydrate in boiling alcoholic solution into the *triazole* derivative,  $\left.\begin{matrix}N{=}CH\\ N(C_6H_3Cl_2)\cdot CS\end{matrix}\right>N\cdot NH_2$, colourless needles, m. p. 153°; under somewhat different conditions, a *product*, $C_9H_6ON_6Cl_2S$, colourless needles, m. p. 196—197° (decomp.) after softening at 191—192°, is obtained, to which the annexed constitution is ascribed.



When acetone is used as solvent in place of alcohol, the action between potassium xanthate and the 2 : 4-dichlorophenylhydrazone of ethyl α-chloroglyoxylate follows a different course and leads to the production of the *sulphide*, $S[C(CO_2Et){:}N\cdot NH\cdot C_6H_3Cl_2]_2$, hygroscopic crystals, m. p. 175—176°, which can also be obtained by the action of ammonium sulphide on the chloro ester.

2 : 4-Dichlorophenylhydrazonopyruvyl chloride does not appear

to be convertible by potassium xanthate into a thiobiazolone; it is transformed by potassium xanthate or colourless ammonium sulphide in the presence of acetone into the *sulphide*,

$S(CAc{:}N{\cdot}NH{\cdot}C_6H_3Cl_2)_2$,

a yellow substance, m. p. 220—222° (decomp.) after becoming black at about 180°. H. W.

o-Hydroxyazoxy Compounds. D. Bigiavi and R. Poggi (*Gazzetta*, 1924, **54**, 114—131).—The authors have investigated the pairs of isomeric azoxy compounds obtained from benzeneazo-*p*-cresol and its derivatives when these are oxidised by means of peracetic acid. That *p*-hydroxyazo compounds exhibit the hydroxylic and not the quinonephenylhydrazonic structure was shown by McPherson (A., 1896, i, 27; 1900, i, 123) and by Willstätter and Veraguth (A., 1907, i, 453), who found that the acyl derivatives of benzeneazophenol are different from the compounds resulting from benzoquinone and the *as*-acylphenylhydrazines. For the corresponding ortho compounds no such difference has been encountered, and their tardy solubility in alkali, their failure to react with ammonia in an anhydrous solvent, and various other physico-chemical considerations incline certain authors (cf. Farmer and Hantzsch, A., 1900, i, 122; Puxeddu and Gennari, A., 1922, i, 587) to prefer the quinonoid to the hydroxyazoic structure for *o*-hydroxyazo derivatives.

The assumption of different constitutions for *o*- and *p*-hydroxyazo compounds seems, however, unwarranted, and, indeed, in many reactions benzeneazo-*p*-cresol behaves similarly to *p*-hydroxyazobenzene. Thus, its ready formation of two isomeric azoxy compounds is not easy to explain on the basis of the quinonoid structure. Moreover, the similarity is borne out by (1) the formation of unstable hydrazophenols when the *o*-hydroxyazo compounds are reduced by either aluminium amalgam in ethereal solution or zinc and ammonium chloride, (2) the formation, by the action of nitrous acid, of a nitro derivative containing the nitro group in the cresol nucleus, and the formation of bisbenzeneazo-*p*-cresol (cf. Puxeddu and Maccioni, A., 1907, i, 798) by the action of a normal diazotate.

The structures of the two benzeneazoxycresols are determined as follows. When treated with bromine, the one, m. p. 125°, yields a dibromo derivative with a bromine atom in each nucleus, since it gives *p*-bromoaniline and 3-bromo-6-amino-*p*-cresol on reduction; the other, m. p. 74°, gives a monobromo derivative and then a polybromo derivative which has bromine in only the cresol nucleus, as the only base volatile in a current of steam formed on reduction is aniline. It may be assumed, therefore, that the former isomeride contains the residue NPh⁚ and is the β-compound, and the latter, O⁚NPh⁚, and is the α-compound. The following observations, confirmatory of these conclusions, have been made.

Nitrous acid does not react with β-benzeneazoxycresol, but with the α-isomeride readily forms a nitro derivative which has the nitro group in the cresol nucleus and in the ortho-position towards the hydroxyl group, as it reacts with diazonium salts to form an azoazoxy derivative. Benzene-α-azoxycresol is readily oxidised by permanganate to *iso*diazobenzene and, probably, to *o*-nitrocresol; with the β-isomeride, the oxidation is extremely slow, although Bamberger gave this reaction as a means of recognising azoxyphenols. The pale yellow α-compound changes moderately rapidly to chestnut-yellow under the influence of light, but the β-isomeride retains its colour almost unaltered. Etherification of the hydroxyl proceeds normally with the α-, but with great difficulty with the β-form. The structure attributed by Baudisch (A., 1917, i, 356) to the β-*o*-hydroxyazoxybenzenes is regarded as unauthorised.

The *nitro* derivative of benzeneazocresol ($N_2 : OH : NO_2 : Me = 1 : 2 : 3 : 5$) crystallises in dark red, lustrous, plush-like needles, m. p. 130°, and is oxidised with difficulty by peracetic acid, yielding a mixture, m. p. 110°, of the two nitroazoxy compounds.

Benzene-α-azoxycresol, $O\!:\!NPh\!:\!N\cdot C_6H_3Me\cdot OH$, forms transparent, orange prisms, m. p. 73—74°, and gives a deep, blood-red coloration with concentrated sulphuric acid. Its *acetyl* derivative separates in yellow needles or transparent, prismatic crystals, m. p. 78—79°, and yields acetylhydrazocresol when reduced by means of aluminium amalgam in ethereal solution. Its *benzoyl* derivative forms pale yellow prisms, m. p. 97—101°.

*Benzene-α-azoxy-*m*-nitro-*p*-cresol*, $O\!:\!NPh\!:\!N\cdot C_6H_2(Me)(OH)NO_2$, crystallises in yellow, silky needles, m. p. 121—122°, and dissolves in alkali hydroxide or carbonate solution to a blood-red solution.

*Benzeneazobenzene-α-azoxy-*p*-cresol*,

$$O\!:\!NPh\!:\!N\cdot C_6H_2(Me)(OH)\cdot N_2Ph,$$

forms long, silky needles, m. p. 148—149°, which are almost black when moistened with benzene, but brilliant chestnut-yellow when dry. With concentrated sulphuric acid, it gives a reddish-brown coloration, and with sodium hydroxide solution containing a few drops of alcohol an intense violet coloration turning to reddish-violet when the liquid is diluted.

*Benzene-α-azoxy-*m*-bromo-*p*-cresol* crystallises in lustrous, sulphur-yellow needles, m. p. 143—144°, and dissolves in sodium hydroxide solution to a bright red solution. When brominated further, it yields the *polybromo* derivative, $C_{13}H_7O_2N_2Br_5$, which crystallises in silky, yellow needles, m. p. 164—165°.

Benzene-β-azoxycresol, $NPh\!:\!NO\cdot C_6H_3Me\cdot OH$, crystallises in lustrous, yellow needles, m. p. 70—72°; its yellow *benzoyl* derivative has m. p. about 56°, and its *acetyl* derivative was obtained only as a dense, non-crystallising oil.

Benzene-β-azoxynitrocresol, $NPh\!:\!NO\cdot C_6H_2Me(OH)\cdot NO_2$, forms yellow, acicular prisms, m. p. 117—119°, and yields aniline when reduced with tin and hydrochloric acid.

Benzene-β-azoxybromocresol, $NPh\!:\!NO\cdot C_6H_2MeBr\cdot OH$, forms chestnut-yellow, silky needles, m. p. 117°.

p-*Bromobenzene-β-azoxybromocresol*, $C_6H_4Br\cdot N\!:\!NO\cdot C_6H_2MeBr\cdot OH$, crystallises in golden-yellow, silky needles, m. p. 166—167°, is turned scarlet and dissolved by alkali hydroxide solution, and yields bromoaniline and bromoaminocresol (cf. Thiele and Eichwede, A., 1900, i, 501) on reduction. T. H. P.

NN′-Dimethylenesulphurous Acid-3 : 3′-diamino-4 : 4′-dihydroxyazobenzene. W. G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1924, **46**, 497—503).—NN′-*Dimethylenesulphurous acid*-3 : 3′-*diamino*-4 : 4′-*dihydroxyazobenzene*, $C_{14}H_{16}O_8N_4S_2$, was isolated by the addition of formaldehyde and sodium bisulphite to the solution of the dihydrochloride of the 3 : 3′-diamino-4 : 4′-dihydroxyazobenzene prepared by the reduction of the corresponding nitro compound in an atmosphere of carbon dioxide. The *sodium*, *magnesium*, and *barium* salts are described. Contrary to expectations, the substance was physiologically inactive. A. B. S.

Absorption Spectra of certain Derivatives of *p*-Cymene. W. C. HOLMES (*J. Amer. Chem. Soc.*, 1924, **46**, 631—635).—The general effect of introducing methyl and *iso*propyl groups into a number of azo dyes of the benzene series is to shift the absorption band towards a region of longer wave-length, the displacement of the maximum being about 10 $\mu\mu$.

Introduction of the *iso*propyl group into Victoria green (malachite green) in the non-aminated nucleus in the *p*-position to the methane carbon atom produces a converging displacement of the two absorption bands in the visible spectrum. Both bands gradually disappear in sulphuric acid solution, and give rise to a new band, that of the *di*-acid salt, in the same spectral region as the second band of the neutral solution. The absorption bands of phenolsulphonephthalein and the homologue containing the *iso*propyl group in the sulphonated residue are practically identical, and absorption measurements in buffered solutions show that as p_H is lowered the transition between the absorption forms characteristic of alkaline and neutral solutions occurs more rapidly with the higher homologue than with the parent substance. S. K. T.

Azo Dyes from *m*-Methylethylbenzene. A. MAILHE (*Bull. Soc. chim.*, 1924, **35**, 382—383).—The following dyes have been prepared from 6-amino-1-methyl-3-ethylbenzene (cf. A., 1921, i, 661): 2-*methyl*-4-*ethyl*-4′-*hydroxyazobenzene*, a brown powder; 1-*methyl*-3-*ethylbenzene*-6-*azo*-β-*naphthol*, a red powder; 1-*methyl*-3-*ethylbenzene*-6-*azo*-β-*naphthylamine*, a maroon powder; 1-*methyl*-3-*ethylbenzene*-6-*azo*-α-*naphthylamine*, a greenish mass; 1-*methyl*-3-*ethylbenzene*-6-*azodimethylaniline*, a brown powder; from Schäffer salt, 1-*methyl*-3-*ethylbenzene*-6-*azo*-β-*naphthol*-6-*sulphonic acid*, dark brown, dyeing maroon on silk; from R-salt, 1-*methyl*-3-*ethylbenzene*-6-*azo*-β-*naphthol*-3 : 6-*disulphonic acid*, a red powder, dyeing silk a fast ponceau; from crocein acid, 1-*methyl*-3-*ethylbenzene*-6-*azo*-β-*naphthol*-8-*sulphonic acid*, a maroon powder, giving maroon shades on silk. From G-salt, 1-*methyl*-3-*ethylbenzene*-6-*azo*-β-*naphthol*-6 : 8-*disulphonic acid*, dark yellow powder, dyeing maroon shades on silk; and from H-acid, 1-*methyl*-3-*ethylbenzene*-6-*azo*-8-*amino*-α-*naphthol*-3 : 5-*disulphonic acid*, reddish-scarlet, giving fast reddish-ponceau shades on silk. R. B.

Colour and Constitution. I. Effect of Isomerism on the Colour of certain Azo Dyes. M. L. CROSSLEY and P. V. RESENVELT (*Ind. Eng. Chem.*, 1924, **16**, 271—273).—Sodium benzeneazo-β-naphthol-6-sulphonate is a reddish-orange dye. If the sulphonic group passes to positions 7 and 8, the colour becomes progressively more yellow. The 3 : 6-disulphonic acid salt is more red, the 6 : 8-disulphonic acid salt more yellow than any of the monosulphonates. Further systematic colour modifications are caused by substitution within the benzene ring. There is also a great difference between the reactivities of the two β-naphtholdisulphonic acids, the presence of the sulphonic group in position 8 appearing to reduce the reactivity of the hydrogen in position 1, by neutralising the effect of the adjacent hydroxyl group. These facts are discussed in terms of the "force-field" and additive theories of chemical reactions. The relation between the effect on colour and the effect on reactivity of the position of the sulphonic group is held to be significant. [Cf. *B.*, 1924, 368.] C. I.

***m*-Nitrocinnamic Acid Hydrazide and its Behaviour with Nitrous Acid.** T. CURTIUS and P. A. BLEICHER (*J. pr. Chem.*, 1924, [ii], **107**, 86—98; cf. A., 1909, i, 838; 1911, i, 682, 814).—The action of hydrazine hydrate on ethyl *m*-nitrocinnamate gives, in addition to the main product of the reaction, m-*nitrocinnamic acid hydrazide*, $NO_2\cdot C_6H_4\cdot CH:CH\cdot CO\cdot NH\cdot NH_2$ (bright yellow, anisotropic plates, m. p. 139°), an isomeric substance, bright yellow needles, m. p. 198°, which with nitrous acid yields a true azide (see following abstract). *m*-Nitrocinnamic acid hydrazide when treated with iodine and sodium hydrogen carbonate in alcoholic solution is converted into a *dihydrazide*,

$$(NO_2\cdot C_6H_4\cdot CH:CH\cdot CO\cdot NH\cdot)_2,$$

pale yellow, prismatic needles, m. p. 279° (decomp.). The *hydrochloride*, tablets, m. p. 212° (decomp.), with benzaldehyde gives *benzylidene*-m-*nitrocinnamic acid hydrazide*, minute needles, m. p. 206·5°, whilst benzoyl chloride yields *benzoyl*-m-*nitrocinnamic acid hydrazide*, $NO_2\cdot C_6H_4\cdot CH:CH\cdot CO\cdot NH\cdot NHBz$, prisms, m. p. 185·5°. With ethyl acetoacetate, *m*-nitrocinnamic acid hydrazide yields the *compound*, $NO_2\cdot C_6H_4\cdot CH:CH\cdot CO\cdot NH\cdot N:CMe\cdot CO_2Et$, white, fibrous needles, m. p. 67·5°, and with phenylthiocarbimide m-*nitrocinnamylphenylthiosemicarbazide*,

$$NO_2\cdot C_6H_4\cdot CH:CH\cdot CO\cdot NH\cdot NH\cdot CS\cdot NHPh,$$

pale yellow plates, m. p. 147°. Sodium nitrite readily converts the hydrochloride into 1-*nitroso*-5-m-*nitrophenyl*-3-*pyrazolidine*, yellow, prismatic plates, m. p. 108° (*ammonium*, *silver*, and *barium* salts described). The silver salt on treatment with ethereal ethyl iodide gives 1-*nitroso*-2-*ethyl*-5-*m*-*nitrophenyl*-3-*pyrazolidine*, greyish plates, m. p. 168°. The ammonium salt of 1-nitroso-5-*m*-nitrophenyl-3-pyrazolidine gives a *picrate*, m. p. 107—108°. The action of bromine on 1-nitroso-5-*m*-nitrophenyl-3-pyrazolidine in acetic acid solution gives 4-*bromo*-3-m-*nitrophenyl*-5-*pyrazoline*, yellow plates, m. p. 188°, only one bromine atom entering the ring, whereas the action of bromine on 1-nitroso-5-phenyl-3-pyrazolidine gives 4 : 4-dibromo-3-phenyl-5-pyrazolone. On boiling with dilute sulphuric acid, the 1-nitroso-5-*m*-nitrophenyl-3-pyrazolidine is converted into 3-m-*nitrophenyl*-4-*isonitroso*-5-*pyrazoline*, orange, silky needles, m. p. 217°.

The isomeric *m*-nitrocinnamic acid hydrazide, of m. p. 198°, gives a *benzylidene* derivative, m. p. 184°, and a *hydrochloride*, m. p. 256° (decomp.). R. B.

m-Nitrocinnamic Acid Azide. T. CURTIUS and E. KENNGOTT (*J. pr. Chem.*, 1924, [ii], **107**, 99—102).—The isomeric *m*-nitrocinnamic acid hydrazide of m. p. 198° formed as a by-product in the action of hydrazine hydrate on *m*-nitrocinnamic ester (see preceding abstract) on treatment with nitrous acid gives m-*nitrocinnamic acid azide*, $NO_2\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot N_3$, colourless, rhombic crystals (m. p. 117—118°, with evolution of gas), which are converted into *m*-nitrocinnamic acid when warmed with alkali. When warmed with *p*-toluidine in alcoholic solution, the azide gives *p*-tolyl *m*-nitrostyrylcarbamide,

$$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot HN\cdot CO\cdot NH\cdot C_6H_4\cdot CH_3,$$

bright yellow needles, m. p. 213—214°. Boiling with water converts the azide into nitrogen, carbon dioxide, and a colourless carbamide (?), m. p. 186°. Boiling with methyl alcohol gives the known methyl *m*-nitrostyrylcarbamate,

$$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot NH\cdot CO\cdot OMe,$$

yellow needles, m. p. 140°, which when boiled with dilute sulphuric acid give *m*-nitrophenylacetaldehyde. The interconversion of *m*-nitrocinnamic acid hydrazide, m. p. 139°, and the isomeric compound, m. p. 198°, can be effected either by heating above the melting point or by warming in alcoholic solution or under pressure. R. B.

Salts with *para*-, *ortho*-, and *meta*-Quinonoid Structure. V. R. CIUSA and G. RASTELLI (*Gazzetta*, 1924, **54**, 72—78; cf. A., 1922, i, 1073).—*p*-Nitrophenylmethylhydrazones,

$$CHR{:}N\cdot NMe\cdot C_6H_4\cdot NO_2,$$

of the following aldehydes have been prepared: *Formaldehyde*, dark yellow crystals, m. p. 153°, separating even from solutions containing the aldehyde in the proportion 1 : 10,000; *acetaldehyde*, yellow needles, m. p. 91°; *butyraldehyde*, yellow crystals, m. p. 05° (?); p-*tolualdehyde*, yellow, tabular crystals, m. p. 150°; o-*nitrobenzaldehyde*, orange-yellow, acicular crystals, m. p. 211—212°; m-*nitrobenzaldehyde*, lemon-yellow crystals, m. p. 250°; p-*nitrobenzaldehyde*, orange-yellow crystals, m. p. 249—250°; *cuminaldehyde*, yellow crystals with violet reflection, m. p. 112°; *dimethylaminobenzaldehyde*, bright red needles, m. p. 193°; *cinnamaldehyde*, dark yellow needles, m. p. 153—154°; *salicylaldehyde*, dark yellow needles, m. p. 150°; p-*hydroxybenzaldehyde*, red crystals, m. p. 204°; *anisaldehyde*, small, yellow crystals, m. p. 155—156°; *protocatechualdehyde*, bright red crystals, m. p. 218°; *vanillin*, m. p. [illegible], existing in yellow and red chromoisomeric modifications; [illegible], yellow crystals, m. p. 190—191°; 2 : 4-*dihydroxy*-[illegible], deep red crystals, m. p. 265°; 2-*hydroxy*-4-*methoxy*-

benzaldehyde, lustrous, yellow needles, m. p. 148°, existing also in a red modification; *furfuraldehyde*, orange-yellow, crystalline plates, m. p. 171°; *pyrrolealdehyde*, bright red, acicular crystals, m. p. 177°; *acetone*, silky, yellow needles, m. p. 54°; cyclo*hexanone*, yellow crystals, m. p. 186°. The *mono*-p-*nitrophenylmethylhydrazone* of *diacetyl* forms brownish-yellow needles, m. p. 154°, that of *acetylacetone*, lustrous, orange needles, m. p. 128°, and that of *acetonylacetone*, yellow needles, m. p. 130°.

Benzaldehyde-p-*nitrophenylethylhydrazone*,

$$CHPh{:}N{\cdot}NEt{\cdot}C_6H_4{\cdot}NO_2,$$

obtained by the action of ethyl iodide on the potassium salt of benzaldehyde-*p*-nitrophenylhydrazone, forms large, yellow crystals, m. p. 134°. When boiled with hydrochloric acid it yields as-p-*nitrophenylethylhydrazine*, $NH_2{\cdot}NEt{\cdot}C_6H_4{\cdot}NO_2$, which crystallises in lustrous, yellow leaflets, m. p. 74°, and energetically reduces Fehling's and ammoniacal silver solutions. p-*Nitrobenzaldehyde*-p-*nitrophenylethylhydrazone* crystallises in yellow needles, m. p. 267°.

Benzaldehyde-p-*nitrophenylbenzylhydrazone*, $C_{20}H_{17}O_2N_3$, prepared from benzyl chloride and the potassium derivative of benzaldehyde-*p*-nitrophenylhydrazone, forms lustrous, yellow, laminar crystals, m. p. 158°, and as-p-*nitrophenylbenzylhydrazine*, $C_{13}H_{13}O_2N_3$, which reduces Fehling's solution and ammoniacal silver solution, yellow needles, m. p. 121°. T. H. P.

[**Aromatic Arsenious Acids.**] A. ALBERT (U.S. Pat. 1472778).—Nitroaminohydroxyacetophenone, when diazotised and treated in alkaline solution with sodium arsenite, yields nitrohydroxyacetylphenylarsinic acid, $CH_3{\cdot}CO{\cdot}C_6H_2(OH)(NO_2){\cdot}AsO_3H_2$, needles, m. p. about 200°. Similarly, *p*-aminobenzophenone yields benzoylphenylarsinic acid, m. p. 195—197°, diaminobenzophenone yields the diarsinic acid compound, m. p. 260°, and *p*-aminobenzaldehyde yields *p*-aldehydophenylarsinic acid.

CHEMICAL ABSTRACTS.

Tin Di*cyclo*hexyl, Hexa*cyclo*hexyldistannane, and other *cyclo*Hexyl Compounds of Tin. E. KRAUSE and R. POHLAND (*Ber.*, 1924, 57, [*B*], 532—544).—An extension of the work on the organo-metallic derivatives of tin (Krause and Becker, A., 1920, i, 340) to the *cyclo*hexyl series. The *cyclo*hexyl bromide used had b. p. 52·5°/13·5 mm., $d_4^{16\cdot8}$ (vac.) 1·3348, $n_D^{16\cdot8}$ 1·49758, whereas *cyclo*hexyl chloride had b. p. 141°/760 mm., $d_4^{20\cdot3}$ 1·0000, $n_D^{20\cdot3}$ 1·46264.

Tin tetra*cyclo*hexyl, $Sn(C_6H_{11})_4$ (cf. Grüttner, A., 1915, i, 335), is prepared by the gradual addition of a solution of stannic chloride in benzene to a solution of magnesium *cyclo*hexyl bromide or chloride in a mixture of ether and benzene. The product is a mixture of tin tetra*cyclo*hexyl, hexa*cyclo*hexyldistannane, and halogenated substances which cannot be separated into its components by crystallisation except with great loss of material; it is therefore converted into the monobromide (see later), which is readily purified and subsequently transformed by magnesium *cyclo*hexyl bromide into the tetra derivative, which crystallises in colourless, quadratic platelets, m. p. 263—264° after slight previous softening (Grüttner gives m. p. 248°).

*Tin di*cyclo*hexyl*, $Sn(C_6H_{11})_2$, prepared from stannous chloride and magnesium *cyclo*hexyl bromide, is an intensely yellow, voluminous powder, melting to a red liquid at 176—178° after darkening at 130°. It is stable in an atmosphere of nitrogen, but gradually oxidises in air, particularly under the influence of light. It is converted by *cyclo*hexyl bromide at 140° into tin di*cyclo*hexyl dibromide. Attempts to convert it into hexa*cyclo*hexyldistannane by means of magnesium *cyclo*hexyl bromide (cf. A., 1920, i, 341) were unsuccessful.

*Hexa*cyclo*hexyldistannane*, $(C_6H_{11})_3Sn\cdot Sn(C_6H_{11})_3$, is prepared by the action of sodium on a solution of tin tri*cyclo*hexyl bromide in boiling xylene. It forms colourless, hexagonal platelets, stable towards light and air, decomp. slightly above 300°. Its molecular weight in concentrated solution corresponds with the formula $[Sn(C_6H_{11})_3]_2$, whereas the simpler molecular form appears to be present in more dilute solution.

*Tin tri*cyclo*hexyl bromide*, $(C_6H_{11})_3SnBr$, prepared from the crude product of the action of magnesium *cyclo*hexyl halide on stannic chloride (see above) by means of bromine in the presence of chloroform or carbon tetrachloride, crystallises in long, colourless prisms, m. p. 77°, decomp. about 280°. The corresponding *iodide* forms colourless, hexagonal plates, m. p. 65°, decomp. about 290°. The *fluoride* forms hexagonal prisms, decomp. about 305°. *Tin tri*cyclo*hexyl hydroxide*, colourless, hexagonal crystals, m. p. 220—222°, is prepared by shaking an ethereal solution of the bromide with an excess of potassium hydroxide solution (15%); when dehydrated, it yields the oxide, $(C_6H_{11})_3Sn\cdot O\cdot Sn(C_6H_{11})_3$. (Tin triphenyl hydroxide, long, hexagonal prisms, m. p. 119—120°, appears to be dehydrated similarly to the *oxide*, $Ph_3Sn\cdot O\cdot SnPh_3$; there is no evidence of the formation of different hydrates.) *Tin tri*cyclo*hexyl chloride*, obtained from the hydroxide and dilute hydrochloric acid, forms long, prismatic rodlets, m. p. 129—130°, decomp. about 286°; with ammonia it appears to yield the *compound*, $(C_6H_{11})_3SnCl,2NH_3$, m. p. 128° (decomp.).

Tin di*cyclo*hexyl dibromide, m. p. 58° (cf. Grüttner, *loc. cit.*), is hydrolysed to the corresponding *dihydroxide* (or *oxide*), a colourless, amorphous powder, m. p. 291° (decomp.) after darkening at 280° and softening at 287°. The corresponding *dichloride*, colourless, asbestos-like needles, m. p. 88—89°, decomp. about 220°, the *difluoride*, a colourless, microcrystalline powder, m. p. 278° after previous softening, and the di-iodide, a colourless, crystalline powder, m. p. 42° (Grüttner, *loc. cit.*, gives m. p. 145°), are described.

The following compounds are prepared by the action of a large excess of the requisite Grignard compound on tin tri*cyclo*hexyl bromide in ethereal solution: *Tin tri*cyclo*hexylmethyl*, $(C_6H_{11})_3SnMe$, a colourless, viscous liquid, b. p. 221°/15 mm., $d_4^{20\cdot7}$ (vac.) 1·1949, $n_D^{20\cdot7}$ 1·53979. *Tin tri*cyclo*hexylethyl*, a very viscous liquid, b. p. [illegible]—228°/15 mm. (partial decomp.), $d_4^{15\cdot9}$ (vac.) 1·1875, $n_D^{15\cdot9}$ 1·53953. [illegible]cyclo*hexyl*, colourless, microscopic crystals, m. p. 191—

192°; 0·65 g. dissolves in 100 g. of ethyl alcohol at 30·4°. *Tin* p-*tolyltri*cyclo*hexyl*, prismatic rodlets, m. p. 111°, which dissolves in ethyl alcohol to the extent of 0·70 g. in 100 g. at 30·4°. *Tin triphenyl*cyclo*hexyl*, colourless needles, m. p. 131—132°, is obtained from tin triphenyl chloride and magnesium *cyclo*hexyl bromide.
H. W.

Peptisation of Gelatin by Mixed Liquids. E. W. J. Mardles (*Biochem. J.*, 1924, **18**, 215—230).—The peptisation of gelatin in mixtures of various solvents has been studied. The solubility of gelatin is greater in mixed liquids than the average value, and under some conditions the solvent power of water can be increased, or not appreciably diminished, by the addition of a non-solvent such as pyridine, glycerol, alcohol, etc. The theory of this phenomenon is discussed. S. S. Z.

Constitution of Proteins. N. Troensegaard and I. Schmidt (*Z. physiol. Chem.*, 1924, **133**, 116—125).—The authors bring forward evidence which they claim lends further support to the view that the protein molecule consists mostly of pyrrole derivatives containing oxygen. Acetylated gliadin, gelatin, and proteolic acid from gliadin were degraded by reduction into various fractions which showed properties characteristic of heterocyclic compounds.
S. S. Z.

Proteins of Oats. H. Lüers and M. Siegert.—(See i, 597.)

Biochemistry.

Influence of Intravenous Injection of Protein on the Respiratory Exchange. E. Amstad (*Biochem. Z.*, 1924, **145**, 168—177).—In dogs, the average normal output of carbon dioxide per kilogram per minute is 9·5585 c.c. and the oxygen intake is 12·94 c.c. Intravenous injection of Ringer solution has a very slight effect in increasing the respiratory exchange; injection of foreign serum (horse) protein first lowers the exchange by 30% of its normal value, but later it rises above normal to the same extent, whilst injection of the serum-proteins of the dog itself produces the same effect as Ringer solution. J. P.

Physiology of Glands. LVIII. Possible Presence of Toxic Substances in the Sera of Thyroid- and Parathyroid-ectomised Animals in Relation to the Respiratory Exchange. L. Asher and K. Jino (*Biochem. Z.*, 1924, **145**, 105—115).—Intraperitoneal injection into rats of 1 to 2 c.c. of the sera of normal or thyroidectomised dogs increases the respiratory exchange, whilst sera from parathyroidectomised dogs with tetany lowers the respiratory exchange. It is concluded that whilst toxic substances are absent in the former case they may be present in the latter. J. P.

Physiology of Glands. LX. Respiratory Exchange of Normal and Splenectomised Rats. L. ASHER and Y. TAKAHASHI (*Biochem. Z.*, 1924, **145**, 130—153).—In general, removal of the spleen from rats diminishes the respiratory exchange, and increases the nitrogen excretion and the response to thyroid feeding as compared with the normal animals. The presence or absence of iron in the dietary has no influence on the respiratory exchange effect. Rats from which the spleen has been removed show a greater susceptibility to lack of oxygen than that shown by normal rats. The results are interpreted in favour of the view that the spleen and the thyroid are mutually antagonistic. J. P.

Physiology of Glands. LXI. Comparison of the Oxygen Consumption of Surviving Excised Mammalian Organs in the Normal Condition and after Thyroid Feeding. L. ASHER and A. ROHRER (*Biochem. Z.*, 1924, **145**, 154—167).—The isolated surviving liver, kidney, and muscle of mice which had been fed on thyroid consumed more oxygen than the same organs from normal animals. The respective figures found for 1 g. of each tissue per hour are: 639 and 784 c.mm., 818 and 941 c.mm., 791 and 985 c.mm. J. P.

Collection and Preservation of Blood Samples for Determination of Carbon Monoxide. R. R. SAYERS, H. R. O'BRIEN, G. W. JONES, and W. P. YANT (*U.S. Public Health Repts.*, 1923, 2005—2011. Reprint No. 863).—A modified Keidel tube method is described for the collection, transport, and storage of samples of 10—15 c.c. of blood in cases of carbon monoxide poisoning. A small vial, well-stoppered with a cork, will serve satisfactorily in emergency. For the inhibition of coagulation, sodium citrate (0·4 to 0·8 %) proved inefficient, sodium or potassium oxalate (0·2%) caused some change in the blood with a slight alteration in the carbon monoxide content, whilst sodium fluoride (0·3%) is recommended as being free from these objections. E. M. C.

Elimination of Carbon Monoxide from Blood by Treatment with Air, with Oxygen, and with a Mixture of Carbon Dioxide and Oxygen. R. R. SAYERS and W. P. YANT (*U.S. Public Health Repts.*, 1923, 2053—2074. Reprint No. 865).—Analyses of blood samples, made in carefully controlled experiments on three subjects, showed that the elimination of carbon monoxide depends on the percentage of oxygen in the air breathed and also on the rate and depth of respiration. Pure oxygen was about four times as efficient as ordinary air, whilst a mixture of oxygen containing 8 to 10% of carbon dioxide was about five to six times as efficient. E. M. C.

Seasonal Changes in the Gases and Sugar of the Blood, and the Nitrogen Distribution in the Blood and Urine of the Alligator. A. HOPPING (*Amer. J. Physiol.*, 1923, **66**, 145—163).—[illegible] capacity of the blood is highest (15·3) in March, and [illegible] in May and June; the oxygen content of the venous blood is lowest (1·8) in May and June and highest (11·0) in January and February. The carbon dioxide capacity and content are higher in spring than in summer or winter. Blood-sugar is high (0·095%) in spring and very low (0·0296%) in late autumn. The main nitrogenous constituent of the urine is ammonia; uric acid is present in the blood and urine in small amounts only.

CHEMICAL ABSTRACTS.

Influence of Oxygen Content on the Hydrogen-ion Concentration of the Blood. J. HOLLÓ and S. WEISS (*Biochem. Z.*, 1924, **145**, 10—13).—The p_H of human oxalated venous blood kept at a constant carbon dioxide content and oxygenated, is lowered by 0·03—0·06.

J. P.

Experimental Tetany. III. Alkalosis and Acidosis. IV. Hydrogen-ion Concentration of the Blood. V. Alveolar Carbon Dioxide Tension. E. W. H. CRUICKSHANK (*Biochem. J.*, 1924, **18**, 47—62).—A change in the acid–base balance in parathyroid tetany, with the production of a condition of alkalosis, is observed in the primary or quiescent stage and is due to CO_2 deficit. With the development of acute tetany, this condition is changed into one of acidosis by the continuous loss of $BHCO_3$ and increase in H_2CO_3. The reaction of the blood as determined from CO_2 dissociation curves changes very slightly, the p_H increasing above normal for the animal by an average of 0·154 during the stage of alkalosis and falling with the introduction of the stage of acidosis. The alveolar CO_2 may fall as low as 1·975%, but with the continued loss of base there is a tendency for it to return towards the normal.

S. S. Z.

Chemical Pathology of Pyloric Occlusion in Relation to Tetany. Chloride, Carbon Dioxide, and Urea Concentrations in the Blood. H. A. MURRAY, jun. (*Arch. Surgery*, 1923, **7**, 166—196).—With stenosis of the pylorus, hydrogen chloride cannot pass into the intestines and be absorbed. It is expelled by vomiting or by gastric lavage. The result is a disturbance in the acid–base balance of the blood and tissues. The blood shows increased carbon dioxide and urea, and decreased chlorine. The most abnormal values found were: CO_2, 107% by vol.; Cl, 2·5 g. per l., and urea, 334 mg. per 100 c.c. of blood. There is a relation between these changes and the tetany which develops in severe cases. It is highly probable that nerve irritation is increased by a fall in the hydrogen-ion concentration of the blood or the sodium : calcium ratio.

CHEMICAL ABSTRACTS.

Nature of the Red Blood-corpuscle. A. GOUGH (*Biochem. J.*, 1924, **18**, 202—214).—The red corpuscle is a fluid droplet the contents of which form a hydrophile colloidal system. The continuous phase (salts and water) constitutes one-third, the dispersed phase (hæmoglobin salts and water) two-thirds of this system. The surface film contains lipoids in a solid state, and all varieties of hæmolysis can be explained as due to disintegration of the envelope of the corpuscle. Crenation is due to protrusion through weak areas in the envelope of the corpuscle. The characteristic shape of the corpuscle is due to tension of liquid surfaces tending to cause a spherical shape and to the repulsive forces between the dispersed particles of the corpuscular contents. S. S. Z.

Adsorption of Protein Degradation Products by Erythrocytes. N. Griasnov (*Biochem. Z.*, 1924, **145**, 63—65).—Contrary to the results of Sbarsky (A., 1923, i, 1252), biological methods of determining fixation reveal no adsorption of diphtheria toxin by erythrocytes *in vitro*. The disappearance of nitrite observed by Sbarsky and attributed by him to adsorption of protein degradation products is ascribed to oxidation by oxyhæmoglobin derived from hæmolysed erythrocytes. J. P.

Hæmoglobin and Methæmoglobin as Oxidative Catalysts. M. E. Robinson.—(See this vol., ii, 320.)

Lævulose in the Blood of the Human Fœtus. A. P. Orr (*Biochem. J.*, 1924, **18**, 171—172).—Human fœtal blood gives the Selivanov reaction, which shows the presence of lævulose. This sugar can also be demonstrated in the blood of the kid immediately after birth. S. S. Z.

Syphilis. V.—VIII. Arsenic Content of the Blood and Spinal Fluid after Neosalvarsan and Salvarsan Treatment. J. A. Fordyce, I. Rosen, and C. N. Myers (*Amer. J. Syphilis*, 1923, **7**, 444—559).—With neosalvarsan, arsenic was found, in quantities of 0·6—83·6 mg. per 100 g. of dried spinal fluid, at some time during the treatment in 22% of the cases; with salvarsan, after combined intravenous and intraspinal injections, arsenic was present in 88% of the fluids up to 73 mg., whereas after injection and drainage, arsenic was present up to 54·3 mg. in 83% of the specimens. The maximum amount of arsenic is present in the blood immediately after intravenous injection of silver salvarsan, but it quickly becomes localised outside of the circulating blood.

Chemical Abstracts.

Hydrogen-ion Concentration of Gastric Contents of Infants. F. L. Babbott, jun., J. A. Johnston, C. A. Haskins, and A. T. Shohl (*Amer. J. Diseases Children*, 1923, **26**, 475—485).—The normal range of the p_H of the gastric contents on the milk test meal at the end of an hour is p_H 3·2—5·0, with 76% of the readings between p_H 3·9 and p_H 4·6. The error of determining acidity of gastric contents from samples rather than from the entire contents is p_H 0·4. The acidity increases with increase in time. The previous type of feeding has no effect on the test meal. Acid production and hydrogen-ion concentration increase with increase of age. A fourfold increase of the concentration of the test meal decreases the hydrogen-ion concentration. A twofold increase of the amount of the test meal causes a stimulation of acid secretion, but a lessened [illegible]. The greater the gastric acidity, the more rapidly the [illegible]

Chemical Abstracts.

Metabolism of Carbohydrates. III. Absorption of Glucose, Fructose, and Galactose from the Small Intestine. J. A. Hewett (*Biochem. J.*, 1924, **18**, 161—170).—Glucose, fructose, and galactose are absorbed from hypotonic solution from the small intestine, the rates of absorption decreasing in the order named. However, when the epithelial lining is destroyed, all three sugars are absorbed at the same rate. The results cannot be explained by osmosis or diffusion only. S. S. Z.

Production of Hypoglycæmia in Experimental Derangements of the Liver. M. Bodansky (*Amer. J. Physiol.*, 1923, **66**, 375—379).—Hyperglycæmia is the initial effect of severe liver damage (severe chloroform or phosphorus poisoning). Subsequently this effect disappears and the blood-sugar falls to subnormal levels. Chloroform and phosphorus are general protoplasmic poisons, and death resulting from such acute poisoning is not due entirely to functional damage of the liver. Chemical Abstracts.

Physiology of Glands. LIX. Influence of Compensation on the Glycosuric Action of Subcutaneous Adrenaline Injections. L. Asher and R. Tsukamoto (*Biochem. Z.*, 1924, **145**, 116—129).—The adrenaline glycosuria of thyroid-fed dogs which react strongly to the treatment, is, in some cases, more rapid but less intense than that of normal animals, but in others the glycosuria may be more intense than that of the normals. The results are explained on the basis of a double functioning of the thyroid hormone. Removal of blood or transfusion of a Ringer gelatin solution after bleeding produces a diminution in the response to adrenaline. J. P.

Preparation of Insulin. Alkaline Extraction of Pancreas. H. W. Dudley and W. W. Starling (*Biochem. J.*, 1924, **18**, 147—150).—By the addition of sodium bicarbonate to the mixture of minced pancreas and alcohol the yield of insulin is increased nearly fivefold. An improved technique for the preparation of insulin hydrochloride through the picrate is also described, whereby at least 90% of the impurities in crude insulin can be removed. 0·2 Mg. of this preparation was found to be a "rabbit unit." S. S. Z.

Mode of Oxidation of Fatty Acids with Branched Chains. III. The Fate in the Body of α-Methylcinnamic Acid, β-Phenyl*iso*butyric Acid, and γ-Phenyl*iso*valeric Acid. H. D. Kay and H. S. Raper (*Biochem. J.*, 1924, **18**, 153—160).—β-Phenyl*iso*butyric acid on oxidation in the body yields benzoic acid. The yield was 77% of the theoretical, assuming that β-oxidation alone had taken place. α-Methylcinnamic acid, which has been isolated as an intermediate product, also yields benzoic acid, but only to the extent of 33% of the amount expected if β-oxidation alone had taken place. No intermediate product could be isolated in this case. No difference was observed in the ease of oxidation in the body of the two isomorphous forms of α-methylcinnamic acid. γ-Phenyl*iso*valeric acid gives rise to phenylacetic acid on oxidation in the body; the yield was not more than 50% of the amount expected if β-oxidation alone had taken place. S. S. Z.

Odd-carbon Fats in the Treatment of Diabetic Ketosis. M. Kahn (*Amer. J. Med. Sci.*, 1923, **166**, 826—833).—An odd-carbon fatty acid has been synthesised (the acid group of stearic acid is replaced by an organic radical and on oxidation the C_{17} acid is produced, which is united with glycerol) which is absorbed to about 90% and is catabolysed without the production of ketones.

Chemical Abstracts.

Metabolism of Milch Cows suffering from Acetonæmia. B. Sjollema and J. E. van der Zande (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 666—668).—Analyses of blood, urine, and milk from cows suffering from acetonæmia show that waste of body fat takes place on a large scale, often about 1 kg. per diem. Lipæmia, glucosuria, and hyperglycæmia do not occur. The total quantity of acetone compounds in the urine may amount to about 120 g. per day. The cholesterol content of the blood is 50% to 100% higher than normal; sometimes it is even higher. The alkali reserve decreases. J. F. S.

Possibility of Influencing Decomposition of Albumin in the Body by Feeding Individual Amino-acids. R. W. Seuffert (*Z. Biol.*, 1924, **80**, 381—404).—Experiments on dogs receiving a diet containing insufficient protein show that whilst the feeding of individual amino-acids of the simplest type or an incomplete mixture of such acids never leads to an increase of body nitrogen or even to nitrogen equilibrium, an appreciable reduction in the daily loss of nitrogen from the body can be achieved by this means, which cannot be accounted for as merely the result of the additional calories brought to the diet by the amino-acids added. These results are checked and confirmed by a consideration of the daily loss of sulphur from the body with and without the addition of amino-acids to the diet. H. C. R.

Choline as a Precursor of Guanidine. Decrease in the Amount of Choline of the Hen's Egg during Incubation. J. S. Sharpe (*Biochem. J.*, 1924, **18**, 151—152).—There is a decrease in choline content of the hen's egg as incubation proceeds. It has been previously shown by Burns that the guanidine content increases during this period. The author suggests that choline is a possible source of guanidine in the animal body. S. S. Z.

Synthesis of Hippuric Acid in the Surviving Kidney of Various Animals and of Man. I. Snapper, A. Grünbaum, and J. Neuberg (*Biochem. Z.*, 1924, **145**, 40—46).—Perfusion of the isolated surviving kidney of the dog, sheep, pig, and man, with blood containing sodium benzoate and glycine, results in the synthesis of hippuric acid. J. P.

Sulphur Metabolism of the Dog. I. Synthesis of Ethereal [illegible] T. S. Hele (*Biochem. J.*, 1924, **18**, 110—119).—[illegible], sodium hydrogen sulphite, and cystine are partly

excreted as ethereal sulphate by the dog when administered by the mouth together with guaiacol carbonate. The sodium sulphate is utilised as readily as cystine or as sodium hydrogen sulphite.
S. S. Z.

Calcium Fixation by Animal Tissues. R. E. Liesegang (*Biochem. Z.*, 1924, **145**, 96—97).—A criticism of the conclusions of Freudenberg and György (this vol., i, 242). J. P.

Mineral Metabolism of the Lactating and Dry Goat. C. H. Hunt, A. R. Winter, J. A. Schultz, and R. C. Miller (*Amer. J. Physiol.*, 1923, **66**, 349—362).—Balances were determined for sodium, potassium, calcium, magnesium, sulphur, chlorine, phosphorus, and nitrogen in dry and lactating goats on various diets, the mineral metabolism being found, in general, to be similar to that of the cow. The calcium and chlorine content of goat's milk is higher than of cow's milk. There is evidence that the calcium in green plants may be more highly dispersed, and hence better assimilated than that of dried feeds. Chemical Abstracts.

Nitrogen and Mineral Salt Metabolism in Avitaminosis. N. Hirabayashi (*Biochem. Z.*, 1924, **145**, 18—31).—In the avitaminosed dog, the body-weight may increase during the first few weeks, usually with increasing nitrogen retention, although towards the end of this period the nitrogen excretion may show an increase. With increasing duration of avitaminosis, the disturbed gastro-intestinal functioning is reflected in diminished body-weight and nitrogen excretion, and in the late stages a temporary increase in the nitrogen retention may set in. The nitrogen excretion is not an indication of the breakdown of nitrogen compounds in the body, since the residual nitrogen of the blood progressively increases in avitaminosis. The phosphorus, calcium, and magnesium balances in avitaminosis are parallel to the diminution in protein metabolism.
J. P.

Properties of certain South African Oils with Respect to Their Content of Vitamin-*A*. E. M. Delf (*Biochem. J.*, 1924, **18**, 93—100).—Sesamé, mafurreira, and castor oils are deficient in vitamin-*A*. Two samples of seal oil have been found to possess considerable growth-promoting properties. Samples of crude whale oil are active inversely to the temperatures used in the extraction. Sperm whale oil obtained from the head is the least active, and that obtained from the blubber is the most active in growth-promoting. When rats are deficient in vitamin-*A*, the addition of vitamin-*C* has a more beneficial effect than when the supply of vitamin-*A* in the diet is adequate. S. S. Z.

Relation of Vitamin-*A* Potency of the Liver Oil to the Sexual Condition and Age of the Cod. S. S. Zilva, J. C. Drummond, and M. Graham (*Biochem. J.*, 1924, **18**, 178—181).—The sexual condition and age of the cod do not influence the vitamin-*A* potency of the liver oil. S. S. Z.

Feeding Experiments in Connexion with Vitamin-*A* and -*B*. V. Orange Juice as a Source of Vitamin-*B*. VI. Ophthalmia in Rats affected with Avitaminosis. VII. The Vitamin Content of Cod-liver Oil and Malt Extract. A. D. STAMMERS (*Biochem. J.*, 1924, **18**, 9—15).—A daily dose of 10 c.c. of orange juice does not contain sufficient vitamin-*B* to promote growth in rats. The susceptibility of rats to keratomalacia varies directly with the amount of vitamin-*A* in the diet. Adult animals are less susceptible. "Cod-liver oil and malt extract" contains sufficient vitamin-*A* and -*B* to provide the necessary stimulus to growth. S. S. Z.

Vitamins. I. L. MARCHLEWSKI and Z. WIEVZCHOWSKI (*Bull. Soc. Chim. biol.*, 1924, **6**, 40—43).—Vitamin-*B* is better extracted from bran by dilute aqueous hydrochloric acid (0·1%) than by alcohol. From this solution, after neutralisation and filtration, addition of an ammoniacal solution of silver nitrate produces a greenish-brown precipitate containing the vitamin. This is dissolved out by hydrochloric acid, and after evaporating to dryness in a vacuum, and dissolving in water, a solution of great potency is obtained. From this solution, on the addition of picric acid, a yellowish-orange compound is precipitated, which may be recrystallised from acetone. A brownish-yellow solution of the vitamin, which has a characteristic odour, is obtained on decomposition of the picrate by dilute hydrochloric acid, and removal of the picric acid with ether. W. O. K.

The Reaction Proposed by Jendrassik as Characteristic of Vitamin-*B*, and its Relation with the Phenolic Grouping. M. N. BEZSSONOFF (*Bull. Soc. Chim. biol.*, 1924, **6**, 35—39).—The solution of ferric chloride and potassium ferricyanide, said by Jendrassik (A., 1923, ii, 892) to turn blue in presence of vitamin-*B*, is turned blue also by *o*- and *p*-phenols. Jendrassik is not justified in his conclusion that vitamin-*B* does not contain a phenolic group. W. O. K.

Antiscorbutic Fraction of Lemon Juice. I. S. S. ZILVA (*Biochem. J.*, 1924, **18**, 182—185).—A great part of the solids of decitrated lemon juice consists of invert-sugar. It is possible to ferment the sugar and thus reduce the solids without appreciably altering the antiscorbutic activity of the solution. The remaining solids seem to consist of substances mainly of a nitrogenous character. Some chemical characteristics of the active fraction are given. S. S. Z.

Conservation of the Potency of Concentrated Antiscorbutic Preparations. II. S. S. ZILVA (*Biochem. J.*, 1924, **18**, 186—187).—Concentrated decitrated lemon juice retains its antiscorbutic potency for five months if stored in acid solution in ampoules in a vacuum. S. S. Z.

[illegible] and Fat-soluble Growth Catalysts (*D*-Vitamins). [illegible] (*Ark. Kemi, Min., Geol.*, 1923, **8**, No. 31, 1—10).—[illegible] pressed yeast and a brewery yeast, by extraction with water, dialysis through collodion membranes, concentration under a pressure of 1 mm., and precipitation by means of alcohol, the author has obtained preparations which effect very marked accelerations of fermentation either by living yeast or by washed dried yeast. With such preparations, however, there exists no parallelism between the influence on the growth of the yeast and that on the fermentation; moreover, no quantitative relationship is observable between the effects produced on the growth of yeast and of mice. In the light of these results the suggestion is made that the letter *D* be retained for growth factors but that D_r and D_m be used to denote the growth substance for rats or mice and for micro-organisms, respectively.

It is proposed further that the name vitamin be reserved exclusively for the following substances which act against definite vitamin-deficiency diseases: vitamin-*A* against rickets; vitamin-*B* against polyneuritis, and vitamin-*C* against scurvy. Substances which accelerate growth but may have nothing further in common with vitamins other than natural occurrence in low concentrations and certain properties relating to sorption, may be designated biocatalysts or growth-substances. In this way, the necessity of classifying Harden's co-zymase, hormones, etc., as vitamins is avoided.

As regards the effect on the growth of mice produced by cod-liver oil, at least one-fifth of the substances causing this effect is found to be transferable to aqueous-alcoholic or aqueous solution. The growth-substance obtained by extracting yeast with water is, however, removed to only a small extent from its concentrated aqueous solution when the latter is shaken with double its volume of a vitamin-free animal oil. T. H. P.

Separation of a Fat Pigment from Accompanying Fat. A. N. CURRIE (*Biochem. J.*, 1924, **18**, 231—234).—The fat is ground with lime and hydrolysed for 10 hours in an autoclave. The adipochrome goes mainly into the aqueous layer. The fatty acids are extracted with distilled water and the aqueous portions are combined and extracted with ether. The aqueous layer, which consists of pigment, salt, and glycerol, is acidified with 20% hydrogen chloride and extracted with ether. The adipochrome goes into the ether. S. S. Z.

Lipochrome of Adipose Tissue in Malignant Disease. A. N. CURRIE (*Biochem. J.*, 1924, **18**, 235—244).—The pigment is an unsaturated aliphatic hydrocarbon and is not related to carotene, xanthophyll, fucoxanthin, the anthocyanins, or the melanins. It is probably derived from the associated fats. The bearing of the adipochrome on the pathology of malignant disease is discussed.
S. S. Z.

Hydrolysis of Hexose-diphosphoric Acid by Various Organs. Y. TAKAHASHI (*Biochem. Z.*, 1924, **145**, 178—181).—Sodium hexose-diphosphate is hydrolysed *in vitro* by the kidneys, spleen, and muscle of the guinea pig, the activity of the organs diminishing in the order given (cf. also Tomita, A., 1922, i, 960).
J. P.

Determination, in Different Organs, of Polonium Injected into an Organism. (MME.) J. S. LATTÈS and A. LACASSAGNE (*Compt. rend.*, 1924, **178**, 771—773; cf. this vol., i, 461).—The distribution, in the rabbit, of polonium, after the injection of the latter, whether intravenously, subcutaneously, or intraperitoneally, is approximately the same. The spleen and kidney are richest in polonium, the former retaining it longer than the latter. The liver, lungs, and especially the heart, rapidly lose their initial polonium. When polonium is injected into a pregnant mouse, the placenta is the organ richest in polonium, which is absent from the amniotic fluid and the fœtus. E. E. T.

Bio-radioactivity. P. BECQUEREL (*Compt. rend.*, 1924, **178**, 795—797).—Nodon's observation of bio-radioactivity (this vol., i, 347; cf. Berthelot, *ibid.*, i, 348) was made by Tommasina in 1904. Radioactive potassium is present in all animal and vegetable protoplasm, and until an improvement in technique enables its detection, the question of bio-radioactivity must remain open.

E. E. T.

Liquid from *Tœnia echinococcus*. O. FLÖSSNER (*Z. Biol.*, 1924, **80**, 255—260).—The presence of considerable amounts of sodium and chlorine and of lesser amounts of potassium, calcium, ammonium, and magnesium in the liquid from *Tœnia echinococcus* was confirmed. Carbonic, sulphuric, and phosphoric acids were also present. The presence of glycogen, betaine, succinic acid, lactic acid, and purine bases was also established. The presence of betaine supports the theory of Kutscher and Ackermann that the metabolism of cold-blooded animals is similar to that of plants. The freedom of the liquid from albumin was confirmed. H. C. R.

Action of Rennet and of Heat on Milk. N. C. WRIGHT (*Biochem. J.*, 1924, **18**, 245—251).—The action of rennet and heat (up to 120° for ½ hour) on caseinogen does not alter the racemisation curves, which suggests that no cleavage takes place in the molecule by the above treatments. Any changes brought about must therefore be of a physical nature. The coloration of autoclaved milk is due to the caramelisation of the lactose, a reaction which appears to be catalysed by the presence of a colloid substrate of calcium caseinogate. The colour of caseinogen precipitated from autoclaved milk is due to adsorption of this pigment.

S. S. Z.

Cholesterol Content of Human Milk. F. W. FOX and J. A. GARDNER (*Biochem. J.*, 1924, **18**, 127—135).—The total cholesterol of 1—12 days' milk is higher than the average of the later period of lactation in the ratios of 1 : 0·59. S. S. Z.

Acidity of Urine Measured by Physico-chemical Methods. C. O. GUILLAUMIN (*Bull. Soc. Chim. biol.*, 1924, **6**, 14—25).—Emphasis is laid on the importance in urine analysis of the determination of [illegible] addition to the usual titration methods. If the [illegible] fractions of the acids present that are ionised [illegible]. It is suggested that the ratio, v/V = c.c. of

N/10-hydrochloric acid required to change p_H from 8·0 to 4·0÷c.c. required to change p_H from 8 to 2·7, might be used to indicate the average degree of dissociation of the organic acids present in urine, but in practice this does not appear to give a trustworthy result.

W. O. K.

Action of Sodium, Potassium, and Calcium Ions and of Uranyl Nitrate on the Spontaneous Rhythmic Movements of the Muscular Skin of the Earth-worm. P. C. HART (*Arch. Néerl. Physiol.*, 1924, 9, 1—29).—The rhythmic movements which preparations of the muscular skin of the earth-worm execute when suspended in Ringer's solution have been studied. The effects of variations in the composition of the solution are, in general, similar to those obtained with isolated organs of other animals. The potassium chloride in the perfusion fluid may be replaced by uranyl nitrate; normal movements are obtained when 10 mg. of uranyl nitrate replace 100 mg. of potassium chloride (cf. *Annual Reports*, 1919, **16**, 148).

E. S.

Action of some Physical and Chemical Agents on the Mobility of Ciliated Infusoria. E. and H. BIANCANI (*Compt. rend.*, 1924, **178**, 800—802).—Ciliated infusoria become permanently immobile under the influence of powerful ultra-violet radiation, a temporary immobility being produced by weak radiation. Salt solutions also induce immobility, isotonic solutions of different salts effecting the change at the same rate. Carbamide, ammonia, and iodine act similarly, the effect being proportional to the concentration. With all the agents mentioned, the dose–time curve is hyperbolic.

E. E. T.

Action of Iodoethylurethane and Iodoethyl Allophanate. B. VON ISSEKUTZ and A. TUKATS (*Biochem. Z.*, 1914, **145**, 1—9).—Ethylurethane, iodoethylurethane, and acetyliodoethylurethane ($CH_3{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}OC_2H_4I$) are increasingly toxic in the order given, whilst compared with the parent urethane, iodoethyl allophanate ($NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}OC_2H_4I$) shows a diminished toxicity. The latter is absorbed in the intestinal tract to a greater extent than the iodine derivatives of the fatty acids, and is excreted in the urine approximately as rapidly and completely as potassium iodide.

J. P.

Pharmacology of the Camphor Group. Comparison of an Isomeric Camphor with Japan Camphor. T. AMAKAWA (*Arch. Exp. Path. Pharm.*, 1924, **101**, 100—126).—The pharmacological action of 3-methyl-5-*iso*propyl-$\Delta^{2,3}$-*cyclo*hexenone (hexeton) is very similar qualitatively to that of camphor, but is several times stronger.

W. O. K.

Bactericidal Action of the Tellurium Derivatives of Aliphatic β-Diketones. II. G. T. MORGAN, E. A. COOPER, and A. W. BURTT (*Biochem. J.*, 1924, **18**, 190—201).—These compounds are extremely germicidal for various strains of bacteria, the bactericidal power being determined by the symmetry of the parent β-diketone and by the presence of methyl and ethyl groups in para-positions within the heterocyclic ring. Tellurium dipropionylmethane, fulfilling both these conditions of chemical structure, is therefore the most active of the series. The bactericidal power of these compounds increases considerably as the homologous series is ascended, until with the presence of an ethyl group and subsequent substitution of one methyl group, a limit is reached, and with further substitution of alkyl groups there is a diminution in efficacy. Position isomerism plays an important part in determining germicidal power. The tellurium compounds lose their strong bactericidal action in the presence of serum, but retain their inhibitory power. In urine, however, their germicidal power is retained. S. S. Z.

Comparative Germicidal Efficiency of Phenol, Mercuric Chloride, and Potassium Mercuri-iodide. J. C. CADORA [in part with R. W. LAMSON] (*J. Amer. Pharm. Assoc.*, 1923, **12**, 401—405).—The values without organic matter were 468·7 for mercuric chloride and 1100 for potassium mercuri-iodide. The minimum lethal dose for the three substances is 0·00035 g., 0·000012 g., and 0·000026 g., respectively. Compared with that of phenol as unity, the coagulating power of mercuric chloride is 55; no coagulating effect was observed with potassium mercuri-iodide. CHEMICAL ABSTRACTS.

Chemotherapeutic Researches in the Series 205 Baeyer. Carbamates of the Aminobenzoylaminonaphthalenesulphonic Acids. E. FOURNEAU, J. TRÉFOUËL, (MME.) J. TRÉFOUËL, and J. VALLÉE.—(See this vol., i, 382 and 504.)

Influence of certain Chemicals on the Rate of Reproduction of Yeast in Wort. N. A. CLARK (*J. Physical Chem.*, 1924, **28**, 221—231; cf. A., 1922, i, 501).—The rate of reproduction of yeast in wort at 25° follows a logarithmic law up to a certain limiting concentration, when the alcohol formed during fermentation begins to have an effect. The influence on this rate of phenol, methyl green, acetone, sodium bicarbonate, and hydrochloric and acetic acids has been studied. In general, the effect is to reduce the rate, which still, however, follows the logarithmic law. With increasing concentration of the poison there is also a resting period of increasing duration before reproduction begins. In every instance, a limiting concentration is reached above which no growth is observed, although it has been shown that this does not necessarily mean that the yeast is killed. When washed free from poison, it is still capable of reproduction. [Cf. *B.*, 1924, 395.] M. S. B.

Optimum Temperature of the Action of a Ferment or Lysin. I. BROWNLEE (*Biochem. J.*, 1924, **18**, 16—18).—The subject is treated mathematically. S. S. Z.

Nature, Constitution, and Mode of Action of Animal Tissue Enzymes. F. MAIGNON (*Compt. rend.*, 1924, **178**, 806—807; cf. this vol., i, 464).—Tissue and pancreatic enzymes, similar with regard to their content of metals, differ in their content of acids (silicic, phosphoric, and arsenic in the former case and hydrochloric in the latter). The tissue enzymes may be written in the form, $(SiO_4)^{II.H.H.II.}$, etc., those of the pancreatic juice as $Cl^{II.}$. The paper contains other (theoretical) matter. E. E. T.

Inactivation of Invertase by Heavy Metals. K. Myrbäck (*Ark. Kemi, Min., Geol.*, 1923, 8, No. 29, 1—37).—Experiments similar to those described by Euler and Svanberg (A., 1920, i, 689) have now been carried out with purer preparations of invertase. The extent to which the enzyme is inactivated by mercuric chloride varies greatly with the purity of the enzyme preparation, since the protein impurities are able to fix mercury and thus protect the enzyme; even with the most highly purified specimens of invertase, the first small additions of the mercury salt are without inactivating action. The purity of an invertase preparation is indicated by: (1) The absence, from the curve connecting relative activity with the proportion of mercuric chloride present, of the characteristic initial inflection that is shown when mercury-fixing impurities are present, (2) the constancy or gradual increase of the unimolecular reaction coefficient, and (3) the non-occurrence of auto-regeneration of the enzymic preparation.

Within the optimum zone, the inactivation by mercuric chloride is virtually independent of the hydrogen-ion concentration and, moreover, unlike what is the case with poisoning by silver, no acidity is capable of annulling the effect of the mercuric salt. Sucrose itself exerts a marked protective action. The mercury equivalent of invertase (per mol. of Hg) in the supposed compound Hg-invertase is calculated to be 3530, and the values $6{\cdot}6 \times 10^{-7}$ and $1{\cdot}0 \times 10^{-7}$ are found by two different methods for the dissociation constant of this compound.

With silver salts also, the amount needed to produce inactivation of invertase becomes very small when the enzyme is highly purified. Cysteine combines with very large proportions of silver, the acidity being without appreciable effect in this case. The poisoning action of copper or lead is similar to that of silver.

In view of the facts that the curve connecting the relative activity of the enzyme with the proportion of mercury present is a dissociation curve, that the acidity is without appreciable influence in the optimum zone, and that the poisoning is affected considerably by the concentration of the sucrose, it must be assumed that mercury forms with the enzyme a dissociating compound; in presence of sucrose, the invertase becomes distributed between the sugar and the mercury. With poisoning by silver, copper, or lead, other conditions must prevail, since the poisoning depends greatly on the acidity and is independent of the concentration of the substrate; in these cases, it is supposed that it is the enzyme-substrate compound which forms with the silver ion a very slightly dissociated salt.

Experiments on the influence of sodium acetate on the action of invertase yielded results similar to those obtained by Fales and Nelson (A., 1916, i, 174) with sodium chloride. T. H. P.

Inactivation of Invertase by Amines. K. Myrbäck (*Ark. Kemi, Min., Geol.*, 1923, 8, No. 32, 1—11).—The inactivation of invertase by *p*-toluidine as a function of the proportion of base present (cf. A., 1923, i, 496) is dependent only in slight degree on the hydrogen-ion concentration of the medium. Assuming that only the free enzyme, and not the enzyme-substrate compound, is able to fix the amine, values are derived for the dissociation constant of the enzyme-amine compound, which are virtually constant for different concentrations of the amine.

The degree of inactivation produced by aniline is not determined solely by the concentration of the base; the more acid solutions cause increased inactivation, which is due to an unknown factor. Ammonia inactivates invertase to as great an extent as do the aromatic amines. T. H. P.

Blood Enzymes. IV. Maltase of Dog's Serum: Influence on Activity of the Reaction of the Medium and of the State of Digestion. A. Compton (*Biochem. J.*, 1924, **18**, 173—177).—The maltase of the blood of the dog, like that of vegetable origin, requires an acid medium for its maximum activity (1·66 c.c. *N*/100 sulphuric acid to 55·5 c.c. of reaction mixture). The activity and the optimum temperature, *i.e.*, 55°, are the same whether the blood is collected during digestion or in the fasting state. S. S. Z.

Takalactase. C. Neuberg and O. Rosenthal (*Biochem. Z.*, 1924, **145**, 185—188).—Takadiastase preparations contain an enzyme—*takalactase*—which hydrolyses lactose practically completely in 216 hours. Lactose osazone is similarly resolved into galactose and glucosazone. In the presence of yeast and takalactase, lactose gives rise to carbon dioxide. J. P.

Fructosediphosphatase in Human Organs. I. E. Forrai (*Biochem. Z.*, 1924, **145**, 48—53).—Many dried human organs are capable of hydrolysing sodium fructosediphosphate, the percentage hydrolysis varying from 66% in the thyroids, to 19% in healthy muscle and 10% in blood-serum. A widespread distribution of fructosediphosphatase is inferred. J. P.

Differentiation of Human Phosphatases. E. Forrai (*Biochem. Z.*, 1924, **145**, 54—56).—From comparative studies of the capacities of extracts of various human organs to hydrolyse glycero-, saccharo-, and fructosedi-phosphoric acids, it is concluded that the phosphatases concerned are different and specific enzymes. J. P.

Determination of the Activity of a Laccase. P. Fleury (*Compt. rend.*, 1924, **178**, 814—816).—The activity of a laccase may be determined by aspirating air through the enzyme preparation in presence of guaiacol, the oxidation of which affords tetraguaiacoquinone. This substance is extracted with chloroform and determined colorimetrically. The lower the concentration of the laccase, the higher is its effectiveness, but, within certain limits, the ordinary linear relation holds between enzyme concentration and amount of substrate decomposed. Between these limits, the above method is accurate. E. E. T.

Mechanism of Oxidation in the Plant. II. Substances Capable of Behaving as Peroxydases. P. H. Gallagher (*Biochem. J.*, 1924, **18**, 29—38).—It is concluded that peroxydase activity is associated with aliphatic aldehydes, which do not act directly but after preliminary conversion by atmospheric oxygen into a substance of oxide nature. Peroxydase preparations prepared by alcoholic precipitation from the juices of vegetables such as the potato, the horse-radish, and the mangold contain a substance or substances of aldehydic nature. Oxides of some heavy metals induce oxidation of guaiaconic acid and of indophenol mixture by peroxide. The chemical nature of peroxydase action is discussed in the light of these results. S. S. Z.

Mechanism of Oxidation in the Plant. III. Peroxydase. Thermostability of the Peroxydase of the Mangold. P. H. Gallagher (*Biochem. J.*, 1924, **18**, 39—46).—Peroxydase of the mangold, inactivated by heat, becomes reactivated when the solution is allowed to remain some time in the cold. This reactivation has been studied quantitatively. The active and the inactivated solutions both contained iron and gave several reactions for aldehyde. Traces of iron added to aqueous solutions of aliphatic aldehydes give rise to an increase of peroxydase activity on standing in the cold. The zymogen of the peroxydase is probably an aldehyde which is activated by the catalytic action of iron after the inactivation by heat. S. S. Z.

Reaction of *Bacillus coli* applied to the Proteolytic Action of Serum (Abderhalden's "Ferments of Defence"). E. Wollman, V. Labernadie, (Mme.) E. Wollman, and (Mlle.) J. Ostrowski (*Ann. Inst. Pasteur*, 1924, **38**, 115—151).—The production of indole from albumin by *Bacillus coli* only occurs after previous proteolysis of the albumin (Wollman, *Compt. rend. Soc. Biol.*, 1919, **82**, 1263). It is thus an indicator of such proteolysis, and may be used instead of the methods of dialysis or optical rotation in carrying out Abderhalden's reaction. The application of this method gave no evidence for the existence of the "ferments of defence" postulated by Abderhalden. W. O. K.

Extraction of Sap from Living Tissues by means of Compressed Air. H. H. Dixon and N. G. Ball (*Sci. Proc. Royal Dubl. Soc.*, 1924, **17**, 263—266).—Liquid was forced out of the wood and leaves of branches by enclosing them in a strong cylinder, in such a way that their cut ends protruded, and increasing the pressure in the cylinder to about 20 atmospheres. This liquid was almost completely free from sugars, except when the leaves had been exposed to toluene vapour. The transport of carbohydrates from the leaves to the stem through the wood involves, in addition to a backward flow through the tracheæ, an increased permeability of the leaf cells. E. M. C.

Physiological Studies on Apples in Storage. J. R. Magness and H. C. Diehl (*J. Agric. Res.*, 1924, **27**, 1—38).—The changes in apples after picking are, in the main, a continuation of those occurring during ripening on the tree. The softening of stored apples is accelerated by increased temperature. The decrease in acidity during storage was practically the same for all varieties of apples, and was independent of the original acidity. Coating the surface of apples with oil or similar material, by reducing the gaseous exchange, retards ripening. So long as anaërobic respiration does not occur, the flavour of the fruit is not detrimentally affected. The higher the temperature of storage, the smaller is the thickness of the coating which will bring about anaërobic respiration and bad flavour. The retardation of ripening appears to be due both to the reduced amount of oxygen and the increased amount of carbon dioxide in the intracellular spaces. Storage of apples in an atmosphere containing up to 10% of carbon dioxide delayed softening, with no apparent loss of quality, but greater proportions caused a bad flavour. A. G. P.

Essential Oil of Manuka (*Leptospermum Scoparium*). R. GARDNER (*J. Soc. Chem. Ind.*, 1924, **43**, 34—35T).—The leaves of the New Zealand wild shrub known as "manuka" yield about 0·45% of greenish-yellow essential oil, d^{15} 0·921, n_D 1·50, b. p. 160—270°/760 mm. The oil consists approximately of phenols (leptospermol), 2·8%; terpenes, 2·8%; cinnamic esters (calculated as ethyl cinnamate), 4·8%; other esters (calculated as $CH_3{\cdot}CO_2{\cdot}C_{10}H_{15}$), 12·9%; semi-solid, non-volatile substances, 7·7%; sesquiterpene, 69·0%. W. P. S.

Protein and Vitamin-*A* Content of the English Walnut. H. L. MIGNON (*Amer. J. Physiol.*, 1923, **66**, 215).—Tannins present in the skins of English walnuts interfere with the extraction of the walnut globulin and constitute a growth-limiting factor in the diets of rats and mice. Vitamin-*A* is present in extremely small amounts. The distribution of nitrogen as amino-acids in walnut globulin, as determined by Van Slyke's method, is: cystine, 0·86; amide, 9·99; humin, 1·84; arginine, 39·13; histidine, 5·74; lysine, 10·61; monoamino-, 30·26; non-amino-, 0·88%.

CHEMICAL ABSTRACTS.

Relation between the Chemical Structure of Bile Acids and their Phytopharmacological and Zoöpharmacological Reactions. D. I. MACHT and O. R. HYNDMAN (*J. Pharm. Exp. Ther.*, 1924, **22**, 483—490).—The inhibition of the growth of seedlings by taurocholic and glycocholic acids appears to be due to the cholic acid in the molecules, since glycine and taurine have little or no action on the growth of seedlings (*Lupinus albus* or *Vicia faba*) or on the reactions of rats in a circular maze, whilst cholic (and also choloidinic) acid is very active. W. O. K.

Saponin of *Panax repens*, Maxim. I. Y. MURAYAMA and T. ITAGAKI (*J. Pharm. Soc. Japan*, 1923, No. 501, 783—789; cf. Inoue, *ibid.*, 1902, No. 242, 356).—After treatment with ether, crushed *Panax repens*, Maxim, was extracted with hot alcohol; from the extract a saponin (5%) was isolated as a white, amorphous powder (m. p. 180—190°), which has a bitter taste.

When shaken with water, it dissolves slightly with foaming; it gives a clear solution on the addition of sodium carbonate. It behaves as an acid, thus supporting the hypothesis of Asahina and Momotani (*ibid.*, 1914, No. 384, 117). It contains 0·33% of ash. When hydrolysed with 3% hydrochloric acid it gave dextrose and a sapogenin (15%). The latter was obtained as white, lustrous needles (m. p. 303—304°). The sapogenin gives the same colour reactions as the saponin, but has no taste. It gives two diacetyl derivatives: one, plates (m. p. 207—210°), and the other, needles (m. p. 257—260°). K. K.

Isolation and Identification of Rutin from the Flowers of Elder (*Sambucus Canadensis*, L.). C. E. Sando and J. U. Lloyd (*J. Biol. Chem.*, 1924, **58**, 737—745).—The yellow pigment "eldrin" from the flowers of the elder (Lloyd, *Eclectic Med. J.*, 1920, **80**, 591) is shown to be identical with rutin from *Eschscholtzia* (Sando and Bartlett, A., 1920, i, 446) in its appearance, composition, products of acid hydrolysis (quercetin, dextrose, and rhamnose), and in its absorption spectrum. The yield of quercetin on hydrolysis is slightly higher than that calculated, owing to the presence of an impurity. G. M. B.

Proteins of Oats. H. Lüers and M. Siegert (*Biochem. Z.*, 1924, **144**, 467—476).—Various protein fractions prepared from oats by Osborne's methods, and belonging to the alcohol-, salt-, and alkali-soluble groups, were examined for their products of hydrolysis. The results are given in tabular form. The differences between the alcohol-soluble proteins of oats and those of the other cereals lie chiefly in the higher cystine and in the medium histidine content. The globulins of oats contain less arginine and decidedly more non-amino nitrogen than the globulins of other cereals. Avenaline, the protein characteristic of oats, is rich in arginine and histidine. Although there are many points of similarity between the nitrogen distribution of the proteins of oats and of other cereals, there is not a complete agreement. The proteins of oats are therefore to be regarded as a distinct group. S. S. Z.

Influence of Phylogeny on the Constitution of the Alkaloids. J. Gadamer (*Pharm. Monatsh.*, 1923, **4**, 157—160; from *Chem. Zentr.*, 1924, i, 56).—Certain families of plants yield characteristic alkaloids. From this fact it is possible to draw conclusions as to the constitution of alkaloids from different species of the same family. G. W. R.

Basic Substances from the Juice of the Alfalfa Plant [Lucerne]. C. S. Leavenworth, A. J. Wakeman, and T. B. Osborne (*J. Biol. Chem.*, 1923, **58**, 209—214).—The filtrate obtained from the press-juice after precipitation by addition of 53% by weight of alcohol (A., 1922, i, 1104) has been hydrolysed by boiling for 12 hours with 25% sulphuric acid and the product examined for basic substances according to Kossel's method. The following substances were isolated: arginine, stachydrin (cf. Steenbock, A., 1917, i, 439), lysine, and a *compound* which was apparently a purine derivative. The latter was obtained from the mercuric sulphate fraction and gave a *picrate*, silky needles, m. p. 298°, and a *hydrochloride* (?), long plates, m. p. about 252°, which contained 31·8% of nitrogen. It is not known whether these bases are present in the press-juice in the free state or whether they are liberated during hydrolysis. Van Slyke's method for analysing the hydrolytic products of proteins is not applicable to the water-soluble constituents of forage plants. E. S.

Extraction of Nitrogenous Constituents from Plant Cells. W. E. TOTTINGHAM, E. R. SCHULZ, and S. LEPKOVSKY (*J. Amer. Chem. Soc.*, 1924, **46**, 203—208).—The investigation deals with the efficiency of various methods of desiccation and extraction as related to the proportions of total soluble nitrogenous compounds and soluble proteins in leaves of the barberry and sugar beet. The influence of freezing and drying on the distribution of nitrogen in plant cells is discussed. The results obtained indicate the desirability of extracting with water as general usage in fractionating the nitrogenous constituents of plant cells; water extracts the greater part of the proteins exposed by crushing the cells of fresh tissue. Chibnall's method of extraction does not sharply separate non-protein from protein nitrogen. F. A. M.

Presence of Vernine (Guanosine) in the Green Leaves and Berries of the Coffee Tree (*Coffea Arabica*, L.) and its Relation to the Origin of Caffeine in this Plant. T. DE A. CAMARGO (*J. Biol. Chem.*, 1924, **58**, 831—834).—A pentoside containing guanine, found in the green leaves and berries of this species, is probably the guanosine previously found in several plants (Schultze, A., 1886, 157, 736) and in nucleic acid (Levene and Jacobs, A., 1909, i, 620). This substance is probably the origin of caffeine in the leaves and berries of the coffee tree. It is transformed by enzymes to guanine, then to xanthine, and finally to caffeine. G. M. B.

Method for Sterile Cultures of the Higher Plants. E. BOBKO (*Z. Pflanz. Düng.*, 1924, **A**, **3**, 41—44).—The apparatus consists of a wide-necked vessel, to hold the nutrient solution, inside the wide neck of which is a piece of net stretched on a frame. The whole is covered with a dome-shaped cap, having cottonwool-plugged tubulures through which seed and sand may be introduced. The lower vessel has a side tube through which an air current or renewed nutrient solution may be passed. The vessel and solution are first sterilised; the seeds are separately sterilised and then introduced on to the gauze and covered with sterile sand. The cover is then removed. A. G. P.

Comparison of the Soil Solution by the Displacement Method and the Water Extract of Alkali Soils. P. L. HIBBARD (*Soil Sci.*, 1923, **16**, 465—471).—When the composition of 1 : 5 water extracts of nine alkali soils was used as a basis for the calculation of the composition of the soil solution, results were obtained which were at variance with those given by an analysis of the solution obtained from the same soil by the displacement method (A., 1921, i, 214). Only in the case of chlorides, nitrates, and sodium were the results given by the two methods in approximate agreement. Calcium and magnesium may be either under- or over-estimated by the water extract method. All the other ions were over-estimated to varying degrees. Analysis of 1 : 5 water extracts of soils is thus liable to give a distorted and, usually, an unfavourable impression as to the composition of the soil solution and the suitability of the soil for plant growth. H. J. P.

Replacement of Soil Potassium. S. C. VANDECAVEYE (*Soil Sci.*, 1924, **17**, 91—96).—Organic manures (clover hay and dung) increased the amount of replaceable potassium in soil (as determined by neutral salt extraction) proportionally to the amounts added. Evidence is given that this liberation of replaceable potassium is largely a chemical phenomenon, and is not the result of biological activities or the production of carbon dioxide in the soil. A. G. P.

Reciprocal Repression Exerted by Calcic and Magnesic Additions upon the Solubility of Native Materials in Surface Soil. W. H. MACINTIRE, W. M. SHAW, and J. B. YOUNG (*Soil Sci.*, 1923, **16**, 449—464).—Lysimeter experiments are recorded in which magnesium and calcium compounds were added to the soil in varying quantities and with the supplementary use of sulphur compounds. In all cases, the addition of lime increased the calcium content of the drainage water and depressed that of magnesium. The reverse occurred when magnesia was substituted for lime. Ferrous sulphate, pyrites, and sulphur each increased the drainage losses of calcium and magnesium; but if used in conjunction with lime, the calcium losses were further increased and those of magnesium lessened. Similarly, magnesia, coupled with either of the sulphur compounds, brought about increased leaching of magnesium, and a depression of the loss of calcium normally occasioned by the sulphur compounds alone. Lime and magnesia in soil slowly revert to an insoluble and unavailable condition. Excessive liming may so depress the solubility of magnesium salts, as to cause a chlorotic condition in plants due to deficiency of magnesium. A. G. P.

Effect of Soil Suspensions on the Solubility of the Sulphate Radical in the System $Ca(OH)_2$–$CaSO_4$–H_2O. W. H. MACINTIRE and W. M. SHAW (*Soil Sci.*, 1924, **17**, 65—89).—In small amounts lime increased the amount of dissolved sulphate in a ferrous sulphate–soil–water suspension. Larger amounts of lime, however, almost eliminated dissolved sulphates from the suspensions, even when a period was allowed, before adding lime, for the reaction between soil and ferrous sulphate to proceed. If the excess of lime were removed from the soil suspension by the addition of sodium carbonate or by carbon dioxide the depressive effect on the solubility of sulphates disappeared. Here also the same effects were observed when the addition of sodium carbonate was delayed. The addition of soil to solutions of calcium sulphate caused the removal of considerable amounts of sulphate from solution. Similar experiments are recorded in which calcium carbonate, magnesium oxide, and carbonate were used in conjunction with ferrous sulphate (cf. *Soil Sci.*, 1923, **16**, 159). Soil structure played an important part in sulphate adsorption. Ignited soil contained more soluble sulphate than the fresh sample, but also adsorbed more sulphate from added solutions, and the effects of lime were accentuated. Greater quantities of sulphate were removed by extracting soil with large amounts of water than by rainwater leaching in lysimeters. A. G. P.

Factors affecting the Growth of Crops on Acid Soils. S. D. CONNER (*Ind. Eng. Chem.*, 1924, **16**, 173—175).—The capacity of a soil to neutralise calcium hydroxide, carbonate, or acetate is a measure of the total acidity, both organic and inorganic. Methods depending on the action of a salt of a strong acid and a strong base, such as potassium nitrate, give a measure of the inorganic acid silicates, but not to any great extent of the organic acids. The expression (inorganic acidity)^2/(organic acidity) gives a better indication of the lime needs of both organic and inorganic soils than that given by any single method of determining acidity. The toxicity of soil acidity may be due to both aluminium ions and hydrogen ions. Some crops, such as maize and radishes, are more sensitive to aluminium ions than to hydrogen ions, whilst others, such as red clover and beets, are more sensitive to hydrogen ions than to aluminium ions. Both phosphates and lime are needed to correct the toxicity of aluminium and hydrogen ions in most acid soils. H. C. R.

Behaviour of Lime in the Soil. O. LEMMERMANN and L. FRESENIUS (*Z. Pflanz. Düng.*, 1924, A, 3, 1—20).—The relationship between the action of various calcium compounds on soils was determined by shaking together soil and various salt solutions. Calcium, supplied to soil as chloride or bicarbonate, was "fixed" largely by base exchange in accordance with the usually accepted views. If slaked lime was used, the calcium was held by adsorption. Carbon dioxide can partly, but not wholly, remove calcium from this adsorbed condition. The addition of calcium hydroxide to soils accelerated the decomposition of organic matter. This occurred even when the amount of calcium hydroxide added was so adjusted that the whole of it would be adsorbed by the soil colloids. The addition of small amounts of lime to soil suspensions caused increased dispersion of the clay, larger amounts producing the normal flocculation. The permeability to water of soil to which successively increasing amounts of lime were added decreased with the smaller additions, and increased as the proportion of lime was further increased. A. G. P.

Determination of Acidity of Soils. R. M. BARNETTE and others.—(See this vol., ii, 347.)

Organic Chemistry.

Primary Products of the Combustion of Carbon. K. Kullgren (*Gas- u. Wasserfach*, 1924, **67**, 226—229).—Carbon dioxide was the main product formed when air, freed from carbon dioxide, was passed over heated retort coke, at 260—410°, but 20% of its weight of carbon monoxide was always present. Dry air reduced the velocity, but did not affect the course of the oxidation. [Cf. *B.*, 1924, 457.] T. S. W.

Sulphochromic Oxidation of Organic Substances and Coals in Presence of Catalysts. D. Florentin (*Bull. Soc. chim.*, 1924, [iv], **35**, 228—230).—The oxidation of the carbon in organic compounds and coals to carbon dioxide by means of the sulphochromic mixture is complete in the presence of a small quantity of a mercury salt. With other catalysts (copper sulphate, silver chromate), or with no catalyst, a certain amount of carbon monoxide is produced also. E. E. T.

Preparation of *n*-Hexane. M. Faillebin (*Bull. Soc. chim.*, 1924, [iv], **35**, 160—161).—Pure *n*-hexane is prepared by the action of pulverised sodium on dry *n*-propyl bromide (Würtz reaction). The sodium is freed from sodium hydroxide by fusion under xylene and is then pulverised under the same liquid. E. E. T.

Conversion of [Solid] Paraffin by Heating under Pressure in the Presence of Hydrogen, Methane, and other Gases. H. I. Waterman and J. N. J. Perquin (*Proc. K. Akad. Wetensch.*, 1924, **27**, 132—139).—The results of further experiments are given. [Cf. *B.*, 1924, 500.] T. H. P.

Constitution of Melene. J. Marcusson and F. Böttger (*Ber.*, 1924, **57**, [*B*], 633—635).—Melene, found by Pictet and Bouvier (A., 1915, i, 513) in coal, in vacuum-tar, in Galician paraffin, and in the products of distillation of beeswax, was assumed to be a solid naphthene, $C_{30}H_{60}$. The authors have now found that Indian paraffin, m. p. 59—60°, consists very largely of melene, which can be readily isolated by crystallisation from benzene and then from light petroleum. It has m. p. 62—63°, d^{65} 0·7913; d^{25} 0·9037; n^{90} 1·4228. Analyses indicate the composition $C_{30}H_{62}$; oxidation with strong hot nitric acid gave a mixture of aliphatic acids, whereas naphthenes under similar conditions gave nitro compounds. Similar differences in behaviour were found on oxidising catalytically with air in presence of manganese dioxide, melene yielding solid fatty acids, whilst naphthenes yielded polynaphthenic acids. Lastly, melene is slowly assimilated at 30° by *Bacterium aliphaticum*, which is incapable of attacking naphthenes. Melene is therefore a paraffin and not a naphthene. F. A. M.

Constitution of Kerogen. J. W. McKinney (*J. Amer. Chem. Soc.*, 1924, **46**, 968—979).—A shale from Albert Mines, New Brunswick, on extraction with acetone yielded 1·36% (calc. on the shale), which is about 4% of the kerogen. The hydrocarbons, amounting to 85% of the extract, on repeated fractionation in a vacuum yielded 15 separate fractions. These, by cooling, were split up into 28 different hydrocarbons consisting of the homologues: $C_{14}H_{30}$ to $C_{26}H_{54}$, $C_{12}H_{24}$ to $C_{24}H_{48}$, $C_{25}H_{48}$, d^{25} 0·8877, $C_{26}H_{50}$, d^{25} 0·8964. Of these, the two last do not appear to have been previously obtained. A. C.

Silver as Catalyst for the Absorption of Ethylene by Sulphuric Acid. W. Lommel and R. Engelhardt (*Ber.*, 1924, 57, [*B*], 848).—The catalytic acceleration of the absorption of ethylene by sulphuric acid by means of silver salts (cf. Gluud and Schneider, this vol., i, 359) has been observed previously (cf. D.R.-P. 393632). The change consists in the successive addition of ethylene to the silver salt and production of ethyl hydrogen sulphate. Addition occurs very rapidly at the atmospheric temperature, whereas the second reaction does not take place with sufficient rapidity below 40°. The absorption of ethylene by aqueous solutions of silver nitrate (10%) and phosphoric acid (4%) may be used for the gas-analytical determination of ethylene; the gas can be removed subsequently by evacuating the solutions with a water-pump. H. W.

Formation of Metallic Acetylides. J. F. Durand (*Bull. Soc. chim.*, 1924, [iv], 35, 161—171).—Acetylene is a very feeble acid (cf. A., 1902, i, 525) and the general methods of preparing salts are now applied to the formation of acetylides. By the action of pure acetylene on solutions of cupric hydroxide in concentrated potassium but not in sodium hydroxide, at 35° a reddish-brown precipitate, CuC_2, was obtained (cf. A., 1897, i, 309) which, immediately after preparation, yielded acetylene with hydrochloric acid or potassium cyanide, but after standing it polymerised and then gave with these reagents an organic, colloidal substance free from copper. Acetylene did not react with copper hydride, but with boiling solutions of zinc ethyl in light petroleum the white zinc acetylide, ZnC_2, was precipitated (A., 1923, i, 449), which gave pure acetylene with water and sodium hydroxide solution; it decomposed (without explosion) at 350° (cf. magnesium and alkaline-earth acetylides).

Solutions of acetylene in acetone gave with mercury ethyl a white, crystalline substance, the precipitation of which was reversible. Boiling solutions of mercury ethyl in light petroleum gave with acetylene gas mercury and carbon, the temperature being too high for carbide formation; boiling solutions of mercury and of lead phenyls in the same solvent gave no result, neither did a benzene solution of lead ethyl. Attempts to prepare aluminium acetylide, $Al_2(C_2)_3$, by the action of acetylene on aluminium carbide at 400—500° failed. E. E. T.

Preparation of Alkyl Chlorides. J. F. Norris and H. B. Taylor (*J. Amer. Chem. Soc.*, 1924, 46, 753—757; cf. A., 1916, i, 461; 1920, i, 831).—Alcohols are converted into the corresponding chlorides when heated for 1 hour under a reflux condenser with concentrated hydrochloric acid and zinc chloride. The lower alkyl halides may be purified from higher polymerides by heating gently under a reflux condenser with concentrated sulphuric acid. The best results are obtained when the molecular ratio of alcohol, hydrogen chloride (as concentrated hydrochloric acid), and zinc chloride is 1 : 2 : 2; yields varying from 60—82% were obtained. Alkyl chlorides were produced from the following alcohols: methyl, ethyl, *n*- and *iso*-propyl, *n*- and *sec*.-butyl, *iso*-amyl, pentan-β-ol, cetyl, β-phenylethyl, γ-phenylpropyl, *m*-nitrobenzyl, and *p*-nitrobenzyl. C. J. S.

Preparation of Various Aliphatic Halides and Halohydrin Compounds. M. T. Bogert and E. M. Slocum (*J. Amer. Chem. Soc.*, 1924, **46**, 763—768).—The method described by Adams and Vorhees (A., 1919, i, 306) for the preparation of alkyl iodides by the use of phosphorus and iodine has been modified so as to avoid the employment of special apparatus. Iodides have been obtained from *n*- and *iso*-propyl, *n*- and *iso*-butyl, and *iso*amyl alcohols (molecular ratio of alcohol, phosphorus, and iodine, 3 : 1 : 3). The trihalides of phosphorus may be used instead of the pentahalides for the conversion of propylene glycol into trimethylene bromide or iodide. Trimethylene bromohydrin and iodohydrin were prepared by passing the dry halogen hydride into propylene glycol; by conducting the operation in the presence of anhydrous benzene, a yield of 90% of the bromohydrin was obtained. A 50% yield of propylene glycol monoacetate was obtained by the action of acetyl chloride on propylene glycol. β-Chloroethyl acetate was obtained in very good yield by the action of a large excess of acetyl chloride on ethylene chlorohydrin. This method was applied to the production of *γ-bromopropyl acetate*, b. p. 88—90°/22 mm., when a yield of 90% was obtained. The best method for the preparation of γ-chloropropyl acetate consists in heating a mixture of propylene glycol, acetyl chloride, and zinc chloride in a sealed vessel for 8 hours at 100°. β-Iodoethyl acetate was obtained in 70% yield from the corresponding chloro compound by the action of excess of potassium iodide in methyl-alcoholic solution; γ-iodopropyl acetate was prepared in 88% yield by passing dry hydrogen iodide into an equimolecular mixture of propylene glycol and glacial acetic acid cooled to 0°. The *methylene ether* of *trimethyl iodohydrin*, $CH_2[O(CH_2)_3I]_2$, b. p. 180—193°/12 mm., was obtained (yield 60%) when a mixture of equimolecular proportions of trimethylene iodohydrin and trioxymethylene was saturated with dry hydrogen chloride, a second molecular proportion of the iodohydrin added, and the reaction completed by warming; it yields formaldehyde and iodopropyl alcohol when boiled with 20% sulphuric acid. C. J. S.

Action of Hydrogen Chloride on Methyl Alcohol. S. R. Carter and J. A. V. Butler (*J. Chem. Soc.*, 1924, **125**, 963).—A solution of hydrogen chloride (400 g.) in methyl alcohol (1 litre) on standing at 18° for 4 days becomes saturated with methyl chloride which is then steadily evolved. The activity of methyl alcohol is thus far greater than that of higher alcohols. F. G. M.

Toxic Properties of Methyl Alcohol. S. Bodforss (*Svensk Kem. Tidskr.*, 1923, **35**, 333—335; from *Chem. Zentr.*, 1924, i, 574—575).—Methyl alcohol is toxic even when pure, and may exert a toxic effect when applied externally. G. W. R.

Determination of Methyl Alcohol. W. M. Fischer and A. Schmidt.—(See ii, 427.)

Detection of Methyl Alcohol. A. Kling and A. Lassieur.—(See ii, 428.)

Unsaponifiable Constituents (Higher Alcohols) of Shark and Ray Liver Oils. III. Y. Toyama (*Chem. Umschau*, 1924, **31**, 61—67; cf. A., 1923, i, 979).—Batyl and selachyl alcohols were prepared from the livers of *Chimæra barbouri* (Garman) and *Narcacion tokionis* (Tanaka). The analyses given by these preparations agreed better with formulæ containing 21 carbon atoms than with the formulæ containing 20 carbon atoms previously assigned to these alcohols. The solid portion of the unsaponifiable matter of these oils contains another alcohol homologous with batyl alcohol which is named *chimyl alcohol* and probably has the formula $C_{19}H_{40}O_3$. This alcohol occurs in the liver oils of several sharks and *Chimæra* and also in many cases is present in greater quantity than batyl alcohol. No trace of the unsaturated alcohol corresponding to chimyl alcohol could be found in these oils. Selachyl acetate had b. p. 242—244°/5 mm., n_D^{20} 1·4550, d_4^{20} 0·9417, iodine value (Wijs) 64·5, saponification value 260·0, molecular refraction 122·8 (calc. 122·0). Selachyl alcohol prepared from the acetate had b. p. 236—239°/5 mm., n_D^{20} 1·4691, d_4^{20} 0·9180, iodine value (Wijs) 79·5, molecular refraction 103·9 (calc. 103·3). The transformation of selachyl alcohol into batyl alcohol on hydrogenation was confirmed. By oxidising selachyl acetate with potassium permanganate in acetic acid solution nonoic acid and an acid of the formula $C_{11}H_{21}O(OAc)_2{\cdot}CO_2H$ were obtained. The formula

$$CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH{\cdot}C_{11}H_{21}O(OH)_2$$

is therefore indicated as representing selachyl alcohol. The principal product obtained on the dry distillation of selachyl acetate is either oleyl alcohol or nonodecyl alcohol. H. C. R.

Methyl Ethyl Sulphate as an Alkylating Agent. T. K. Thayer (*J. Amer. Chem. Soc.*, 1924, **46**, 1044—1046).—*Methyl ethyl sulphate*, b. p. 198—200°/742 mm., is prepared by adding ethyl chlorosulphonate (1·3 equivalents) to a suspension of sodium methoxide in dry ether. The yield was 19·7% of the theoretical. The alkylating powers of methyl sulphate and methyl ethyl sulphate were compared by alkylating solutions of phenol. Using methyl sulphate, the yield of anisole was 74·2% of the theoretical. With methyl ethyl sulphate, 56·7% of the phenol was converted into anisole and 13·4% into phenetole, which shows that the methyl group has the greater alkylating power. A. C.

Laboratory Preparation of Ethyl Sulphate. E. V. LYNN and H. A. SHOEMAKER (*J. Amer. Chem. Soc.*, 1924, **46**, 999—1001).—A mixture of alcohol (50 g.) and concentrated sulphuric acid (104·5 g.) is allowed to drop on to anhydrous sodium sulphate (90 g.) in a flask fitted with a condenser and arranged for vacuum distillation. The flask is kept at 155—165° (optimum temp.) by an oil-bath and the pressure maintained at 20—45 mm. The mixture enters through a capillary tube at about 120—150 drops per minute. The time of distillation for the above quantities is 1 to 1½ hours. The ethyl sulphate is separated from the alcohol in the distillate, washed with dilute sodium carbonate and then with cold water, and dried over anhydrous sodium sulphate. The product (32·6 g.) is almost pure and is neutral to litmus. A. C.

Action of Mixed Dialkyl Sulphates on Mixed Organo-magnesium Compounds. L. BERT (*Compt. rend.*, 1924, **178**, 1182—1184).—Methyl, propyl, *iso*propyl, *n*-butyl, and *iso*amyl ethyl sulphates were prepared by the action of ethyl chlorosulphonate on the corresponding sodium alkoxide. Bushong's observations (A., 1903, i, 732) on the *iso*propyl and *iso*amyl compounds were confirmed and the following constants are given for the methyl compound: b. p. 85°/15 mm., $d^{16\cdot5}$ 1·228, $n_D^{16\cdot5}$ 1·399. *Ethyl propyl sulphate* is a colourless oil, b. p. 107—108°/18 mm., $d^{16\cdot5}$ 1·140, $n_D^{16\cdot5}$ 1·411; *ethyl* n-*butyl sulphate*, a colourless oil, b. p. 117—118°/20 mm., d^{18} 1·112, n_D^{18} 1·415. Magnesium phenyl bromide reacts with all the above substances, yielding toluene in the case of methyl ethyl sulphate and ethylbenzene with the other four. H. J. E.

Explosive Decomposition of Glyceryl Trinitrate. AUDIBERT (*Compt. rend.*, 1924, **178**, 1167—1169).—The decomposition of glyceryl trinitrate on explosion takes place in two stages; the first (explosive reaction) is represented by the equation $C_3H_5O_9N_3 \longrightarrow 2CO+CO_2+2\cdot5H_2+1\cdot5N_2O+1\cdot75O_2+21$ cal., whilst the second (residual reaction) gives rise to the final system, $3CO_2+2\cdot5H_2O+1\cdot5N_2+0\cdot25O_2$, with a further evolution of 319 cal. Neither reaction is instantaneous; completion of the second depends on the conditions of reaction. H. J. E.

Action of some Halohydrins on Normal Sodium Phosphate in Aqueous Solution and on some Glycerophosphates. O. BAILLY and J. GAUMÉ (*Compt. rend.*, 1924, **178**, 1191—1193).—Similar results to those obtained with the chlorohydrin of glycerol and normal sodium phosphate (Bailly, A., 1916, i, 113) were observed in the cases of the bromohydrin and the iodohydrin, but the two stages of the reaction were more clearly differentiated. The authors have prepared the *normal glycerophosphates* of *sodium, potassium*, and *strontium* and the *acid glycerophosphates* of *barium, strontium*, and *calcium*. H. J. E.

Ease of Oxidation of Organic Substances at the Ordinary Temperature. M. GOMPEL, A. MAYER, and R. WURMSER (*Compt. rend.*, 1924, **178**, 1025—1027).—Solutions of formic, acetic, propionic, oxalic, succinic, citric, lactic, and pyruvic acids, glycine, alanine, and dextrose when shaken with blood charcoal at 40° evolve carbon dioxide. The rate of evolution of the gas is considerably affected by the presence and concentration of hydrogen ions, especially in the case of the acids of greater dissociation constant. The authors point out the biological significance of their observations. H. J. E.

Mechanism of Oxidation Processes. VII. H. Wieland (*Annalen,* 1924, **436**, 229—262).—I. [With A. Wingler.]—**Catalytic Fission and Oxidation of Keto-acids.**—Under the influence of palladium black, vegetable charcoal, and animal tissue, dilute aqueous solutions of keto-acids are hydrolysed with loss of carbon dioxide (cf. A., 1915, i, 354, 1046; 1916, i, 772). In this way, oxalacetic acid yields pyruvic acid, pyruvic acid gives acetic acid, malic acid yields acetic acid, and α-keto-β-phenylpropionic acid gives phenylacetic acid, benzaldehyde, benzoic acid, and oxalic acid. The reaction takes place in an atmosphere of nitrogen, provided that a hydrogen acceptor such as methylene-blue or *p*-benzoquinone is present. Traces of acetaldehyde were detected in experiments with pyruvic acid and washed animal tissue. The mechanism of the action is discussed.

II. [With H. Lörenskiold.]—**Mode of Reaction of Hydrogen Peroxide. Critical Experiments on Thunberg's Theory of Carbon Dioxide Assimilation** (cf. A., 1923, i, 1271).—On distilling hydrogen peroxide with pure lead carbonate the authors could detect no formaldehyde in the distillate, and Thunberg's results are considered to be due to the presence of traces of acetate in his lead carbonate. Only the slightest traces of formaldehyde were formed when formic acid was distilled with hydrogen peroxide, and the observation of Wislicenus (A., 1918, i, 472) that formic acid is formed in the oxidation of bicarbonates with hydrogen peroxide has been verified under conditions precluding the possibility of formic acid being introduced from atmospheric sources.

The results obtained by Dakin (A., 1908, i, 74) and Neuberg (A., 1915, i, 214, 215) in the oxidation of organic acids with hydrogen peroxide have been confirmed, but it is shown that the presence of ferrous iron is not essential. Comparative experiments with acetic acid and glycollic acid showed that formaldehyde was formed very much more rapidly in the latter case, and the view is expressed (cf. A., 1901, i, 310) that glycollic acid is the first stage in the oxidation of acetic acid with hydrogen peroxide. [Cf. i, 612.]

Glyoxylic acid, on oxidation with the same reagent, yields carbon dioxide and formic acid (cf. A., 1904, i, 474). In the case of butyric, crotonic, and β-hydroxybutyric acids, in addition to the aldehyde, considerable quantities of acetone are formed. Cinnamic acid yields chiefly the aldehyde; the saturated acid yields the aldehyde and ketone in approximately equal amounts. Malic acid, like succinic acid, is oxidised to acetic acid.

III. [With H. Rau.]—**Decomposition of Dihydroxyethyl Peroxide with Alkali** (cf. A., 1923, i, 650).—The decomposition of dihydroxyethyl peroxide with sodium hydroxide in the presence of silver below 0° follows the course: OH·CHMe·O·O·CHMe·OH $\longrightarrow$ $2Me·CO_2H+H_2$, to the extent of 40%, whereas at 15° only 30% of the peroxide decomposes in this way. The alternative decomposition: OH·CHMe·O·O·CHMe·OH $\longrightarrow$ $Me·CO_2Na+CHO·Me+2H_2O$, has therefore the greater temperature coefficient. [Cf. also A., 1920, i, 709.] R. B.

Purification of Acetic Acid. K. J. P. Orton and A. E. Bradfield (*J. Chem. Soc.*, 1924, **125**, 960—961).—Acetic acid is best purified by distillation with chromium trioxide (2 g. per 100 c.c. of acid); the first 5% is rejected. The main fraction (85—90%), if distilled through an 8-pear still-head, melts at 16·2—16·4°, and is free from impurities which react with bromine. F. G. M.

Identity of Phocenic and Valeric Acids. E. André (*Compt. rend.*, 1924, **178**, 1188—1191).—Synthetic and natural valeric acids were found to have boiling points almost identical with those of specimens of phocenic acid obtained from dolphin-head oil and from porpoise fat. Amides of all four specimens exhibited almost identical melting points, which were unchanged on mixing the substances in pairs. The statement that phocenic acid is a mixture of butyric and caproic acids (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," 5th ed., i, 152) is thus regarded as incorrect. H. J. E.

αβ-Dihalogenated Amylacrylic Acids. C. Moureu and M. H. Schindler (*Bull. Soc. chim.*, 1924, [iv], **35**, 171—178).—*αβ-Dibromoamylacrylic acid* [*αβ-dibromo-Δ^α-octenoic acid*], a colourless liquid which will not crystallise, b. p. 144° (3 mm.), d_4^{18} 1·6444, $n_D^{19·5}$ 1·5320, is prepared by direct addition of bromine in chloroform solution to amylpropiolic acid. The *potassium, silver,* and two unstable *lead* salts, $(C_5H_{11}·CBr{:}CBrCO_2)_2Pb$ and

$$(C_5H_{11}·CBr{:}CBrCO_2)_2Pb·PbO,$$

are described. *αβ-Di-iodo-Δ^α-octenoic acid*, white needles, m. p. 47·5—49·5°, decomp. 100°, is prepared by direct addition of iodine to amylpropiolic acid, excess halogen being removed by sulphur dioxide. The *potassium* and *lead* salts are described; neither is very stable in solution. A basic *lead* salt was also obtained. The dihalogenated amylacrylic acids are less stable than the corresponding halogenated acrylic and crotonic acids. Attempts to separate the acids into isomerides by fractional distillation of the dibromo acid, fractional crystallisation of the di-iodo acid, and fractional crystallisation and precipitation of the salts all failed. The dibromo acid may be a mixture of two isomerides, one being in excess, and the crystals of the di-iodo acid may be a pure form. E. E. T.

Action of Carbonyl Chloride on Metallic Derivatives of Monosubstituted Acetylenes. I. Action of Carbonyl Chloride on Sodium *tert.*-Butylacetylide. M. P. Ivitzky (*Bull. Soc. chim.*, 1924, [iv], **35**, 357—360).—The sodium derivative of *tert.*-butylacetylene reacts readily with carbonyl chloride in ethereal solution yielding *trimethyltetrolyl chloride* [*γγ-dimethyl-*

Δ^{α}*-pentinoyl chloride*], $CMe_3{\cdot}C{:}C{\cdot}COCl$, b. p. 46·5—47·5°/16 mm., which, on hydrolysis, yields $\gamma\gamma$-dimethyl-Δ^{α}-pentinenoic acid, b. p. 106—107°/10 mm., m. p. 48—49°. The acid chloride can also react with a second molecule of the acetylide, and the unsaturated ketone, *bis-$\gamma\gamma$-dimethyl-Δ^{α}-butinenyl ketone*, $(CMe_3{\cdot}C{:}C)_2CO$, colourless crystals, m. p. 66·5°, is obtained as a by-product in the reaction. If the carbonyl chloride is added at once to the sodium *tert.*-butylacetylide, a violent reaction takes place, and after decomposition of the product with water, *tri-$\gamma\gamma$-dimethyl-Δ^{α}-butinenyl carbinol*, $(CMe_3{\cdot}C{:}C)_3C{\cdot}OH$, colourless crystals, m. p. 102·5°, is obtained. By the action of sodium *tert.*-butylacetylide on acetone a substance, m. p. 102·5°, was obtained in almost quantitative yield.
R. B.

Bauer Oil, the Higher-boiling Residue from Molasses Fusel Oil. A Source of Capric [Decoic] Acid. C. S. MARVEL and F. D. HAGER (*J. Amer. Chem. Soc.*, 1924, **46**, 726—730).—A dark reddish-brown oil, b. p. 130—235°/35 mm., obtained as a residue during the distillation of molasses fusel oil, consisted of the ethyl esters of decoic, lauric, myristic, and palmitic acids, and a little unsaponifiable matter. This forms an additional source for the preparation of decoic acid, which occurs only in small quantities in the common fats. [Cf. *B.*, 1924, 438.] C. J. S.

Glycerides of Fats and Oils. XI. Glycerides of Palm Kernel Oil. A. BÖMER and K. SCHNEIDER (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 61—89).—Five almost pure mixed glycerides were isolated from a sample of palm kernel oil by repeated fractional crystallisation from acetone, and were identified as decoylomyristoolein, myristodilaurin, laurodimyristin, palmitodimyristin, and myristodipalmitin. The first two of these glycerides were present in considerable amount, the third only in small amount, and the last two in very small amount, comprising the most difficultly soluble glycerides in the oil. It is very unlikely that stearic acid is present in the glycerides of palm kernel oil, and hexoic acid was not present in the sample investigated. It is uncertain whether decoic acid was present or not. H. C. R.

Chemical Composition of Sesamé Oil. G. S. JAMIESON and W. F. BAUGHMAN (*J. Amer. Chem. Soc.*, 1924, **46**, 775—778).—Sesamé oil having the characteristics d_{25}^{25} 0·9187, n^{20} 1·4731, acid value 1·4, iodine value (Hanus) 110·8, saponification value 189·3, unsaponifiable matter 1·73%, acetyl value 9·8, Reichert-Meissl value 0·11, Polenske value 0·15, was found to contain the glycerides of the following acids in the proportions indicated: oleic (48·1%), linolic (36·8%), palmitic (7·7%), stearic (4·6%), arachidic (0·4%), and lignoceric (0·04%). C. J. S.

Oils and Fats from the Seeds of Indian Forest Plants. VI. Oil from the Seeds of *Aleurites montana*, Wilson. R. M. PARKER, M. G. RAU, W. A. ROBERTSON, and J. L. SIMONSEN (*Indian Forest Records*, 1923, **10**, 11—22).—The oil had the following characteristics: d_{15}^{15} 0·9467, n_D^{15} 1·494, acid value 3·4, saponification value 203, unsaponifiable matter 0·6%, iodine value 141·4, insoluble fatty acids 94% (solidifying point 54—54·5°). The principal fatty acid present in the oil was β-elæostearic acid (m. p. 73°). The α-isomeride was apparently completely absent. The β-elæostearic acid was brominated in chloroform solution and an unstable *dibromo* derivative (m. p. 95°) obtained. On bromination in acetic acid solution, a mixture of a solid and a liquid tetrabromo acid was obtained. The solid product, needles, m. p. 115°, was not identical with the tetrabromo acid from linolic acid. The liquid acids present in the oil were identified as oleic and linolic acids; linolenic acid was absent. H. C. R.

Oils and Fats from the Seeds of Indian Forest Plants. VII. Oil from the Seeds of *Salvia plebeia*, R. Br. M. G. Rau and J. L. Simonsen (*Indian Forest Records*, 1924, **10**, 23—26).—The ground seeds on extraction with cold benzene gave 11% of an oil having the following characters: d_{30}^{30} 0·934, n_D^{30} 1·4832, acid value 6·0, saponification value 195·0, unsaponifiable matter 0·02%, acetyl value nil, iodine value 131·1, Reichert Meissl value 1·3, solidification point of the insoluble fatty acids 10·5—11°. Stearic acid was the only saturated acid present. Linolenic acid, linolic acid, and oleic acid were identified in the oil. H. C. R.

Tung Oil. A. Eibner, O. Merz, and H. Munzert (*Chem. Umschau*, 1924, **31**, 69—82).—Tung oil contains 75% of glyceryl α-elæostearate, which changes under the influence of light into the solid geometrical isomeride, glyceryl β-elæostearate. Both the α- and the β-triglycerides increase in weight at about the same rate when exposed to the air in thin films. After standing for 10 months in a closed brown glass bottle, β-elæostearin became insoluble in acetone and no longer melted, but charred at about 265°. Both α- and β-elæostearic acids, m. p. 48° and 72°, respectively, were prepared from tung oil which had stood for some time, by extracting with ethyl alcohol and fractionally crystallising the extract from this solvent at about 0°. Another acid (m. p. 106·5°), giving the reaction of azelaic acid with ferric and mercuric chlorides, was obtained from the residue insoluble in cold alcohol, and is presumably a cleavage product obtained from elæostearic acid. The difference in the drying properties of α- and β-elæostearic acids was investigated by exposing thin layers of the acids to the air. After 8—10 days, the α-acid was transformed into a clear yellow syrup, whilst the β-acid remained unchanged for 14 days and was only transformed into a clear yellow, viscous syrup after 4 weeks' exposure. Only two of the three possible geometrical isomerides of elæostearic acid have been obtained. It is considered that the α-acid is probably the *cis-cis* form and the β-acid the *cis-trans* form. Bromination of both α- and β-acids yields the same tetrabromide (m. p. 114°). The transformation of the α into the β geometrical isomeride, on treatment with bromine, is considered to be a peculiarity confined to compounds containing two double linkings separated by two methylene groups, a constitution which explains the high reactivity of elæostearic acid. Evidence is adduced in favour of the view that the conversion of the α- and the β-acid plays very little part in the mechanism of the drying of tung oil, which appears to be a colloidal phenomenon involving transformation from the sol to the gel form rather than a case of molecular polymerisation. H. C. R.

Hydrate of Bismuth Lactate. E. MOLES and R. PORTILLO (*Anal. Fis. Quím.*, 1924, **22**, 133—143).—Bismuth lactate obtained by the action of lactic acid on bismuth hydroxide contains water of hydration corresponding to the formula $C_6H_9O_6Bi,7Aq$. In solution, it behaves as a non-electrolyte, as is shown by cryoscopic and conductivity determinations. The solution, on keeping, deposits the anhydrous salt which has a smaller solubility than the hydrated salt. The reaction appears to be autocatalytic. G. W. R.

Sebacic Acid. E. BŒDTKER (*J. Pharm. Chim.*, 1924, **29**, 313—319).—Ricinoleic acid, when distilled with an excess of sodium hydroxide, gives sebacic acid, octyl alcohol, methyl hexyl ketone, and a viscous, brown residue. From the latter have now been isolated stearic acid, m. p. 69·2°, an acid, m. p. 81—82°, which is either ricinic acid, $C_{18}H_{34}O_3$, or hydroxystearic acid, undecenoic acid, $C_{11}H_{20}O_2$ (formed by the pyrogenic decomposition of the ricinoleic acid), and finally an asphaltic resin. The maximum yield of sebacic acid (33 g. from 100 g. of ricinoleic acid) is obtained by heating sodium ricinoleate with one equivalent of sodium hydroxide. F. G. M.

Resolution of Racemic Malic Acid and the Preparation of *d*-Malic Acid. E. DARMOIS and J. PERIN (*Bull. Soc. chim.*, 1924, [iv], **35**, 353; cf. A., 1923, i, 299).—The *d*-malic acid obtained from active chlorosuccinic acid by treatment with silver nitrate according to Walden's process is now shown to be partly racemised, about 25% of the product consisting of the *l*-acid. By the addition of ammonium molybdate, it is possible to isolate successively the lævo- and dextro-rotatory forms of the ammonium dimolybdomalate, $2MoO_3,C_4H_6O_5,2NH_3$, the lævo-form crystallising first. Racemic ammonium dimolybdomalate does not appear to exist at the experimental temperatures, 16—20°, the crystals obtained when the compound is prepared from *r*-malic acid consisting of the *d*- and *l*-dimolybdomalate in equal proportions. A satisfactory method of converting the dimolybdomalonates into the corresponding malic acids has not yet been found, the product obtained from ammonium *l*-dimolybdomalonate being *l*-malic acid and not the *d*-form as was expected. R. B.

Resolution of Inactive Malic Acid into Optically Active Forms. H. D. DAKIN (*J. Biol. Chem.*, 1924, **59**, 7—12).—From a solution of cinchonine and inactive malic acid in molecular proportions in hot methyl alcohol or acetone, *cinchonine* l-*malate* separates in very good yield, and may be completely purified by crystallisation from methyl alcohol, or from water; from the [illegible] it separates in clear, hard prisms, m. p. 197—198°,

$[\alpha]^{19}_D$ +146° (in water). The methyl alcohol or acetone filtrate from the lævo salt is concentrated and water added occasionally; the residue is allowed to crystallise from water, when *cinchonine* d-*malate* (+$2H_2O$) is obtained as fine rosettes of clear, silky, prismatic needles, m. p. (hydrated) 106°, (anhydrous) 125—135°, $[\alpha]^{18}_D$ +153° (in water). On decomposition of the cinchonine salts with ammonia, *d*-malic acid, m. p. 99—100°, $[\alpha]^{19}_D$ +2·33°, and *l*-malic acid, m. p. 99—100°, $[\alpha]^{18}_D$ −2·31°, were obtained.

W. O. K.

Phosphor-Emetic [Potassium Phosphoryl Tartrate]. I. H. STERNLIEB (*Bull. Acad. Sci. Roumaine*, 1923, **8**, 211—214; cf. Costeanu, following abstract).—Crystals of potassium phosphoryl tartrate, $CO_2K{\cdot}CH(O{\cdot}PO){\cdot}CH(OH){\cdot}CO_2H,0{\cdot}5H_2O$, are prepared by dissolving 2 parts of phosphorus trioxide and 3 parts of potassium hydrogen tartrate in 16 parts of water and, with constant stirring, heating to the boiling point. The sparingly soluble, small, white crystals, having $[\alpha]^{15°}_D$ +80·62°, which separate, lose the water of crystallisation at 110°, and at 200° form a hygroscopic anhydride, m. p. 242°. S. K. T.

Emetics [Cæsium Antimonyl Tartrate].—N. D. COSTEANU (*Bull. Acad. Sci. Roumaine*, 1923, **8**, 215—218; cf. Sternlieb, preceding abstract).—Three methods are given for the preparation of the hitherto unknown *cæsium emetic* (*cæsium antimonyl tartrate*), $CO_2Cs{\cdot}CH(O{\cdot}SbO){\cdot}CH(OH){\cdot}CO_2H,0{\cdot}5H_2O$. (1) By the action of diantimonyl tartaric acid (prepared by dissolving freshly-precipitated antimony oxide in cold tartaric acid solution and precipitating with alcohol) on normal cæsium tartrate solution, partly precipitating with alcohol, warming the mixture and cooling again. (2) By the interaction of cæsium chloride and silver antimonyl tartrate. (3) By boiling a solution of cæsium hydrogen tartrate with antimony oxide.

Cæsium antimonyl tartrate forms transparent, orthorhombic prisms, *d* 2·27, [α] +79·21°, loses its water of crystallisation at 100°, and, at 200°, forms an anhydride. The aqueous solution dissolves iodine, any remaining undissolved assuming a golden colour; it yields precipitates with silver and lead nitrates, ferric chloride, and mineral acids. S. K. T.

Action of Triphenylmethyl Chloride on Free Sulphydro Groups. E. BILLMANN and N. V. DUE (*Bull. Soc. chim.*, 1924, [iv], **35**, 384—390; cf. A., 1905, i, 625; 1906, i, 625; 1908, i, 142).—The action of triphenylmethyl chloride or bromide on xanthylacetic acid proceeds in accordance with the scheme:

$$OEt{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CO_2H + CPh_3Br \longrightarrow CPh_3{\cdot}S{\cdot}CO{\cdot}S{\cdot}CH_2{\cdot}CO_2H + EtBr$$
$$\longrightarrow COS + CPh_3{\cdot}S{\cdot}CH_2{\cdot}CO_2H.$$

The following compounds have been obtained: *Triphenylmethylthiolacetic acid*, $CPh_3{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, brilliant pointed prisms, m. p. 162·5—163°, which is not decomposed by warm dilute sodium hydroxide, but on treatment with bromine yields dithiolacetic acid and triphenylmethyl bromide; α-*triphenylmethylthiolpropionic* *acid*, microscopic white crystals, m. p. 151°; β-*triphenylmethylthiolpropionic acid*, white, microscopic crystals, m. p. 208—209°; *triphenylmethylthiolsuccinic acid*, fine octahedra, m. p. 186—187° (decomp.).

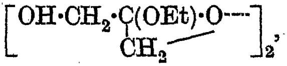
In a similar way, the action of triphenylmethyl chloride on free xanthic acid in benzene solution yields triphenylmethyl xanthate, $CPh_3{\cdot}S{\cdot}CS{\cdot}OEt$, large, yellow crystals, m. p. 139°, in a 97% yield. Free thiolbenzoic acid in toluene solution gives triphenylmethyl thiobenzoate, $C_6H_5{\cdot}CO{\cdot}S{\cdot}CPh_3$, m. p. 187·5—188°, in 85% yield (cf. A., 1901, i, 636; 1913, i, 1335) and thiocyanic acid in ethereal solution gives an 89% yield of triphenylmethyl thiocyanate, $NCS{\cdot}CPh_3$, m. p. 137·5%. R. B.

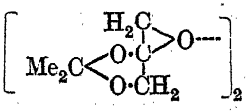
Alleged Reduction of Carbon Dioxide to Formaldehyde by Hydrogen Peroxide, and the Assimilation Hypothesis of T. Thunberg. A. Bach and M. Monosson (*Ber.*, 1924, **57**, [*B*], 735—738; cf. A., 1923, i, 1271).—The production of traces of formaldehyde on distilling basic lead carbonate with hydrogen peroxide was confirmed. The authors show, however, that the formaldehyde is not produced from the lead carbonate itself, but from the small amounts of organic preservatives (*e.g.*, acetanilide) used to stabilise the hydrogen peroxide, which are catalytically oxidised by the latter in presence of lead. Control experiments using purified materials gave completely negative results, whilst the addition of a little acetanilide led at once to the production of formaldehyde. The addition of barbituric acid, however, gave no trace of formaldehyde. Thunberg's assimilation hypothesis is therefore devoid of foundation. [Cf. i, 606.] F. A. M.

Electrolytic Oxidation of Formaldehyde. C. del Fresno (*Anal. Fis. Quim.*, 1924, **22**, 121—132; cf. Müller and Hochstetter, A., 1914, ii, 615; Müller, A., 1920, i, 709).—The author has studied the electrolytic oxidation of formaldehyde in solutions of sodium hydroxide with electrodes of platinum, copper, and silver, respectively. Curves are drawn showing the relation between anode potential and current intensity. The results are in agreement with the theories of Müller. In each case where the anode potential exceeds a certain value the current intensity decreases, and at the same time there is a discontinuity in the potential, which becomes more positive. The passage of a current begins at much lower potentials in alkaline solutions containing formaldehyde than in solutions of sodium hydroxide alone. With electrodes of copper and silver, oxidation of formaldehyde occurs accompanied by evolution of hydrogen (dehydroxidation) at low potentials, whilst at high potentials, as is the case also with platinum electrodes, oxidation occurs without evolution of hydrogen. The mechanism of the oxidation is discussed. G. W. R.

Production of Acetone by the Action of Potassium Acetate on Acetic Anhydride. E. Luce (*Bull. Soc. chim.*, 1924, [iv], 35, 179—183).—The amount of acetone produced by refluxing acetic anhydride and potassium acetate for 30 hours at 170—180°

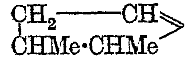
is not influenced by the presence of acetic acid. The yield of acetone is small, owing to polymerisation and to loss through carrying away by the carbon dioxide produced. The latter is prevented by special apparatus, and the yield then becomes 24% of the theoretical. No carbon monoxide is formed; sodium acetate cannot replace the potassium salt (cf. T., 1886, **49**, 317). Since the reaction is slow and at first no carbon dioxide is evolved, elevation of the temperature simply causing acetic anhydride to distil over; it probably follows the course $Ac_2O+Me\cdot CO_2K=(AcO)_2CMe\cdot OK=COMe_2+CO_2+Me\cdot CO_2K$. When potassium acetate is replaced by the butyrate, acetone and methyl propyl ketone are obtained. E. E. T.

Dihydroxyacetone. H. O. L. Fischer and H. Mildbrand (*Ber.*, 1924, **57**, [*B*], 707—710).—Dihydroxyacetone has been prepared in the unimolecular *form* [needles or rhombs, m. p. (indefinite) 65—71°] by the distillation of bimolecular dihydroxyacetone under greatly diminished pressure and immediate cooling of the distillate. It is converted by acetic anhydride and pyridine into the unimolecular diacetate, m. p. 42—45 [Dimroth and Schweizer (A., 1923, i, 745) give m. p. 46—47°]. With acetone in the presence of anhydrous copper sulphate, it yields the corresponding bimolecular *dïisopropylidene ether*, needles, m. p. 165·5—167·5°, to which the annexed constitution is ascribed. Freshly distilled dihydroxyacetone is converted by ethyl orthoformate in alcoholic solution in the presence of ammonium chloride into the corresponding *ethylcycloacetal*, 
$\left[\begin{array}{l}OH\cdot CH_2\cdot C(OEt)\cdot O—\\ \qquad\quad CH_2\end{array}\right]_2$, m. p. 126°. H. W.



Pennone [ββγγ-**Tetramethylpentane**-δ-**one**]. R. Locquin and W. Sung (*Compt. rend.*, 1924, **178**, 1179—1182; cf. A., 1923, i, 433, also Richard, A., 1911, i, 6).—In dehydrating ββγδ-tetramethylpentane-γδ-diol, only 6—7% of the substance is transformed into hexamethylacetone. The chief product (76%) is *ββγγ-tetramethylpentane-δ-one*, $C_9H_{18}O$, m. p. 63—64°, b. p. 167·5°/746 mm. (*oxime*, m. p. 125°, b. p. 215—220°; *semicarbazone*, m. p. 207—208°). On reduction by sodium and alcohol, the ketone, which the authors designate as *pennone*, yields the corresponding secondary alcohol, *pennol*, m. p. 50°, b. p. 179—180°. Oxidation of the ketone or alcohol yields *ααββ-tetramethylbutyric acid*, m. p. 200° (*ethyl* ester, a mobile liquid, b. p. 168—169°/746 mm.). H. J. E.

Reactions Relating to Carbohydrates and Polysaccharides. VIII. Electrolytic Reduction of Carbonyl Derivatives. H. Hibbert and R. R. Read (*J. Amer. Chem. Soc.*, 1924, **46**, 983—999).—Various ketones and aldehydes were reduced by an electrolytic method in order to compare the activities of the carbonyl group. The carbonyl derivative was added to an electrolyte (usually 2*N*-sulphuric acid with or without alcohol) in the cathode compartment, and caused a fall in the cathode potential varying with the ease or difficulty with which the substance underwent reduction. In the case of aldehydes, this depended on (*a*), whether saturated or unsaturated: the fall was 0·12 volt for *n*-butaldehyde and 0·58 volt for crotonaldehyde; (*b*) the length of the chain; (*c*) the spatial relation of the atoms: the values for acetaldehyde, propionaldehyde, *iso*butaldehyde, and *n*-butaldehyde were 0·30, 0·30, 0·17, 0·12 volt, respectively; (*d*) character of groups in molecule: substitution of hydrogen by hydroxyl is shown by comparing *n*-butaldehyde 0·12 volt, with acetaldol, 0·25 volt. Ketones brought about a much smaller effect: dimethyl, methyl ethyl, and methyl propyl ketone showed 0·06, 0·06, and 0·04 volt, respectively. To compare the "current efficiencies," which were found to run parallel to the lowering of cathode potentials, the hydrogen absorbed was plotted against the total hydrogen as measured in a coulombmeter in series with the experimental cell. The reduction products of crotonaldehyde were found to be different from those obtained by chemical reduction. The main fraction consisted of 2:3-*dimethyl*-Δ^5-cyclo*pentene*-1-*aldehyde*:



$$\begin{matrix} CH_2\text{——}CH \\ | \\ CHMe{\cdot}CHMe \end{matrix}\!\!>\!C{\cdot}CHO$$

, b. p. 170—175° (*semicarbazone*, white needles, m. p. 185—187°). Little or no dipropenyl glycol was formed. Dextrose could not be reduced to mannitol. The aldehydes investigated (apart from crotonaldehyde) were in all cases reduced to the corresponding alcohols, acetaldol to a glycol. The ketone reduction products were oily and had a pungent odour; they were not isolated. It is concluded that in the case of carbonyl derivatives such as the carbohydrates, anhydro-sugars, and polysaccharides, the determination of the two factors described results in values lying too close together to be of service as a means of distinguishing between the residual valencies of the carbonyl groups; and, further, that refinements in the measurements of the factors appear of little use owing to the limits imposed by the non-reproducibility of the cathode. A. C.

Course of the Mutarotation of Dextrose. H. v. Euler, K. Myrbäck, and E. Rudberg (*Ark. Kemi, Min., Geol.*, 1923, 8, No. 28, 1—9).—According to Euler and Hedelius (A., 1920, i, 712), the reaction constant for this change is 6×10^{-3} in a solution having p_H 5 at 20°, and measurements made by Michaelis give the value $6{\cdot}6 \times 10^{-13}$ for the acid dissociation of dextrose at the same temperature. From these results, the concentration of the intermediate product or of the reacting ions is calculated to be $3{\cdot}7 \times 10^{-8}$. Since Michaelis employed dextrose solutions containing α- and β-dextroses in equilibrium in the known proportions, the authors have carried out experiments to ascertain if α-dextrose behaves, with respect to salt-formation, differently from β-dextrose or from the equilibrated mixture; no appreciable difference is found in this regard. Further, the degree of hydrolysis of the dextrose-alkali salt varies inconsiderably with the temperature. [H. v. Euler and Rudberg, A., 1923, ii, 840.] T. H. P.

Action of Guanidine on Dextrose in the Presence and Absence of Oxygen. E. J. Witzemann (*J. Amer. Chem. Soc.*, 1924, [illegible]).—Morrell and Bellars (T., 1907, 91, 1010) have shown that guanidine is comparable with sodium and potassium hydroxides with regard to the velocity of hydrolysis of ethyl acetate. The results now described show that guanidine is also comparable with these bases in its action on dextrose both in the presence and absence of air or hydrogen peroxide. Guanidine causes polymerisation accompanied by yellowing more rapidly than potassium hydroxide, but this action is much less influenced by temperature than in the instance of the latter base. C. J. S.

Optical Behaviour of βε-Anhydroglucose, of βε-Anhydrogluconic Acid, and of βε-Anhydromannonic Acid. P. A. Levene (*J. Biol. Chem.*, 1924, **59**, 135—139).—Stereochemical considerations lead to the expectation that epichitose (βε-anhydroglucose) would not be able to form an oxide ring structure, and that it therefore exists in the aldehydic form. It is actually found that it is decolorised very rapidly by permanganate. Chitonic acid and chitaric acid do not exhibit mutarotation, probably because, likewise, lactone formation is not possible. W. O. K.

Preparation of α-Mannose. II. P. A. Levene (*J. Biol. Chem.*, 1924, **59**, 129—134).—A solution of mannose (100 g.) in water (25 c.c.) is cooled to 0°, and cooled glacial acetic acid (400 c.c.) is added. The crystals of α-mannose which separate are filtered after 4—5 hours, and subsequently extracted eight times with alcohol (80% by weight, 200 c.c., for each 100 g. of sugar). From optical observations on the mutarotation of α-mannose it is found that $K_1+K_2=0{\cdot}0054$, in 80% alcohol at 25°, and 0·0029 in water at 1·5°, where K_1 is the rate of conversion of the α- into the β-form, and K_2 the rate of the reverse reaction. From similar observations on β-mannose, $K_1+K_2=0{\cdot}0029$, in water at 1·5°, and 0·00575 in 80% alcohol at 25°. Measurements of solubility give $K_1=0{\cdot}00193$ and $K_2=0{\cdot}00041$. These results elucidate the discrepancy previously reported (Levene, this vol., i, 15). W. O. K.

α-Mannose Penta-acetate. P. A. Levene (*J. Biol. Chem.*, 1924, **59**, 141—144).—Acetylation of α-mannose in pyridine with acetic anhydride results in the formation of α-mannose penta-acetate, m. p. 64°, $[\alpha]_{D}^{17}$ +57·6°, identical with the penta-acetate obtained by Hudson and Dale (A., 1915, i, 502) by the action of zinc chloride on β-mannose penta-acetate. W. O. K.

Three Isomeric Crystalline Tetra-acetylmethyl-*d*-mannosides. J. K. Dale (*J. Amer. Chem. Soc.*, 1924, **46**, 1046—1051).—*α-Tetra-acetylmethyl-*d*-mannoside*, m. p. 65°, $[\alpha]_{D}^{20}$ +49·1°, was prepared by acetylating methyl-*d*-mannoside with acetic anhydride and sodium acetate. β-*d*-Mannose penta-acetate dissolved in glacial acetic acid saturated with hydrobromic acid yields a syrupy product containing bromine, which is converted by silver carbonate in the presence of methyl alcohol into *γ-tetra-acetylmethyl-*d*-mannoside*, m. p. 105°, $[\alpha]_{D}^{20}$ −26·6°. This compound possesses properties not generally characteristic of the acetylated glucosidic derivatives of the sugars. When subjected to alkaline hydrolysis, only three out of the four acetyl groups are removed, although the whole four are removed by acid hydrolysis. On treating its solution in methyl alcohol with hydrogen chloride, a rapid change in rotation occurs and an apparent equilibrium is reached in a few minutes at $[\alpha]_D^{20}$ +10·4°. The solution at this stage was neutralised, and yielded a third isomeride, β-*tetra-acetylmethyl*-d-*mannoside*, m. p. 162°, $[\alpha]_D^{20}$ −47·0°. Although the yield was only 7% of the theoretical, attempts to extract further crystalline substances were unsuccessful.

The close parallel in specific rotation and behaviour on hydrolysis between these isomerides and the three crystalline triacetylmethyl-*l*-rhamnosides recently prepared by Fischer, Bergmann, and Rahe (A., 1921, i, 94), is pointed out. A. C.

Isomeric Diacetonemannoses [Mannose Di*iso*propylidene Ethers]. P. A. Levene and G. M. Meyer (*J. Biol. Chem.*, 1924, 59, 145—149).—Methylation of diacetonemannose by methyl iodide and silver oxide resulted in the formation of a *methyldiacetonemannose*, b. p. 115°/1·2 mm., $[\alpha]_D^{20}$ +23° (in *s*-tetrachloroethane), which on hydrolysis by alcoholic hydrochloric acid yields mannose. Methylation by sodium and methyl iodide (cf. Freudenberg and Hixon, A., 1923, i, 1179) results in the formation of a methyldiacetonemannose, $[\alpha]_D^{20}$ −42·2° (in *s*-tetrachloroethane). These may be more or less pure samples of the α- and β-forms of α-methyl-βγεζ-diacetonemannoside, as from α-methylmannoside a diacetone-α-methylmannoside, b. p. 105°/0·5 mm., $[\alpha]_D^{20}$ +34·9°, was obtained. W. O. K.

Specific Rotations of Hexonic and α-Aminohexonic Acids and of their Salts. P. A. Levene (*J. Biol. Chem.*, 1924, 59, 123—127).—The following specific rotations are given: gluconic acid, $[\alpha]_D^0$ 0·0°; mannonic acid, $[\alpha]_D^0$ +15·6°; gulonic acid, $[\alpha]_D^0$ +1·6°; galactonic acid, $[\alpha]_D^0$ −8·0°; allonic acid, $[\alpha]_D^0$ −10·0°; altronic acid, $[\alpha]_D^0$ +8·0°; whilst only sufficient idonic acid was available to ascertain that it is in all probability dextrorotatory. On comparison of these figures with those previously given for their sodium salts, phenylhydrazides, and amides, it appears that the rotation of the free acid is in the opposite sense from that of the derivatives. The following figures are also given: chitosaminic acid, $[\alpha]_D^0$ −1·3° in 5% sodium hydroxide solution (c = 5·0%), −15° in 2·5% hydrochloric acid; epichitosamic acid, $[\alpha]_D^0$ −5·0° in 5% sodium hydroxide solution (c = 5%), +10° in 2·5% hydrochloric acid solution; "dextro-*d*-xylos-α-aminohexonic acid," $[\alpha]_D^0$ −16° in 5% sodium hydroxide solution (c = 2·5%), +14° in 2·5% hydrochloric acid solution; "lævo-*d*-xylos-α-aminohexonic acid," $[\alpha]_D^0$ +2·0° in 5% sodium hydroxide solution (c = 2·5%), −11° in 2·5% hydrochloric acid solution; chondrosaminic acid, $[\alpha]_D^0$ −15° in 5% sodium hydroxide solution (c = 2·5%), −17° in 2·5% hydrochloric acid solution; epichondrosaminic acid, $[\alpha]_D^0$ −1·8° in 5% sodium hydroxide solution (c = 2·5%), +8·0° in 2·5% hydrochloric acid solution, "dextro-*d*-ribos-α-aminohexonic acid," +2·0° in 5% sodium hydroxide solution (c = 2·5%), +12·5° in 2·5% hydrochloric acid solution; "lævo-*d*-ribos-α-aminohexonic acid," $-15°$ in 5% sodium hydroxide solution ($c = 2·5\%$), $-26·0°$ in 2·5% hydrochloric acid solution. W. O. K.

Relation between Rotatory Power and Structure in the Sugar Group. IV. Two Isomeric Crystalline Hexa-acetates of *d*-α-Mannoheptose. C. S. Hudson and K. P. Monroe (*J. Amer. Chem. Soc.*, 1924, **46**, 979—983).—Acetylation of *d*-α-mannoheptose by adding the sugar to gently boiling acetic anhydride containing sodium acetate resulted in the isolation of a crystalline *hexa-acetate*, m. p. 106°, $[\alpha]_D^{20}$ $+24·2°$ in chloroform. It was transformed by hot acetic anhydride and zinc chloride into a strongly dextrorotatory syrup from which a second *hexa-acetate*, m. p. 139—140°, $[\alpha]_D^{20}$ $-31°$ in chloroform, crystallised. From a comparison with the dextrose penta-acetate, it is inferred that the first hexa-acetate is a β-form and that the main (strongly dextrorotatory) amorphous product is the α-form. Comparison of the hexa-acetates with the galactose penta-acetates (A., 1916, i, 546) indicates that the compound, m. p. 106°, and the strongly dextrorotatory amorphous product are probably β- and α-forms of the butyleneoxide type, whereas the substance, m. p. 139—140°, is a β-form of some other type. A. C.

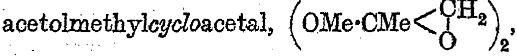
Polysaccharides. VIII. Molecular Structure of β-Hexa-amylose. J. C. Irvine, H. Pringsheim, and J. Macdonald (*J. Chem. Soc.*, 1924, **125**, 942—947).—Karrer and Bürklin's statement (A., 1922, i, 435) that triamylose and β-hexa-amylose are identical is disproved by the conversion of the latter on exhaustive methylation into the crystalline β-*hexa(trimethylamylose)*, $C_{54}H_{96}O_{30}$, m. p. 102—105°, thus confirming the view of Pringsheim and Dernikos (A., 1922, i, 632). β-Hexa(trimethylamylose) on hydrolysis in methyl-alcoholic solution containing 1% of hydrogen chloride gave an equilibrium mixture of α- and β-trimethylmethylglucoside, which on further hydrolysis in 8% aqueous hydrochloric acid gave only 2 : 3 : 6-(βγζ-)trimethylglucose.
F. G. M.

Synthesis of Amygdalic Acid from Gentiobiose. G. Zemplén (*Ber.*, 1924, **57**, [*B*], 698—704).—Gentiobiose octa-acetate is converted by successive treatment with methyl-alcoholic sodium methoxide solution, sodium hydroxide, and methyl sulphate, and finally with silver oxide and methyl iodide, into heptamethyl methylgentiobioside, long, colourless needles, m. p. 109°, $[\alpha]_D^{11}$ $-22·39°$ in water, $[\alpha]_D^{16·5}$ $-20·89°$ in alcohol [Haworth and Wylam (T., 1923, **123**, 3124) give m. p. 106°, $[\alpha]_D$ $-33·9°$ in water, $-29·9°$ in alcohol]. On hydrolysis, it yields 2 : 3 : 5-trimethyl β-methylglucoside and 2 : 3 : 5-trimethylglucose. Gentiobiose octa-acetate is transformed by glacial acetic and hydrobromic acids in the presence of chloroform into acetobromogentiobiose,

$$C_{12}H_{14}O_3(OAc)_7·Br,$$

m. p. 131—133·5°, $[\alpha]_D^{19}$ $+111·8°$ in chloroform, which is converted by silver *dl*-mandelate into *hepta-acetylgentiobiosidyl mandelate*, $C_{12}H_{14}O_{11}Ac_7·CO·CH·PhOH$, small, colourless needles, m. p. 209° (decomp.) after softening at 205°, $[\alpha]_D^{17·5}$ $-9·73°$ in chloroform, and hepta-acetylamygdalic acid, m. p. about 90°, $[\alpha]_D^{15}$ $+6{\cdot}25°$ or $+10{\cdot}55°$ in chloroform. In its main features, synthetic hepta-acetylamygdalic acid closely resembles the product derived from amygdalin, but an exact comparison is rendered difficult by the amorphous nature of both compounds. A wide discrepancy is observed only in the specific rotation, which is attributed to the incomplete racemisation of the mandelic complex in the conversion of amygdalin into hepta-acetylamygdalic acid and to a partial resolution of silver *dl*-mandelate into its active components during the preparation of the synthetic acid (cf. Karrer and co-workers, A., 1921, i, 260). H. W.

Starch Grains. L. Rosenthaler (*Schweiz. Apoth.-Ztg.*, 1923, **61**, 654—659; from *Chem. Zentr.*, 1924, i, 451—452).—Starch grains from different plants may in some cases be distinguished by their behaviour towards methylene-blue, naphthylene-blue, and neutral-red, respectively. Observations are also recorded on the behaviour of different kinds of starch grains towards peptising reagents, acids, and alkalis. Whilst the results are of value for analytical purposes, they are nevertheless in many cases influenced strongly by experimental conditions. G. W. R.



Iodo Compounds of Simple αβ-*cyclo*Acetals of the Type of Starch Iodide. M. Bergmann (*Ber.*, 1924, **57**, [*B*], 753—755).—A solution of acetolmethyl*cyclo*acetal, $\left(\mathrm{OMe{\cdot}CMe}<\overset{\mathrm{CH_2}}{\underset{\mathrm{O}}{|}}\right)_2$, in methyl alcohol is converted by iodine and potassium iodide below 0° into the *compound* $C_8H_{16}O_4I_4,KI$, very unstable, bluish-black prisms, m. p. 50—52° when rapidly heated. The methyl*cyclo*acetal of acetoin gives a similar, but even less stable, *compound*, dark, steel-blue prisms. The formation of starch iodide is attributed to the presence in starch of similar oxygen rings, which cause addition of iodine and potassium iodide owing to their pronounced residual affinity. The polyamyloses do not behave in this manner. H. W.

Polymerisation of the Cellulose Molecule. P. Bary (*Compt. rend.*, 1924, **178**, 1159—1161).—A theoretical paper in which the two different types of reaction undergone by cellulose involving (*a*) no depolymerisation and a colloidal resultant, or (*b*) depolymerisation with a resultant which is less colloidal in its nature than cellulose, are considered. Cellulose is represented, not as $(C_6H_{10}O_5)_m$, but as $(C_6H_{10}O_5)_m,H_2O$, where *m* is very large, and the suggestion is put forward that hydrolysis and depolymerisation are effected by hydration of one of the oxygen linkings in the unit structure of the molecule. H. J. E.

Cellulose in Coal. F. Schulz and J. Hamackova (*Bull. Soc. chim.*, 1924, **35**, [iv], 183—187).—Cellulose was extracted from various recent lignites by Schorger's method (*J. Ind. Eng. Chem.*, 1917, 9, 556). The maximum content was 12% (referred to the weight of lignite less moisture and ash). The cellulose, a greyish-white mass in the crude state, was recognised by hydrolysis to a hexose and by conversion to cellobiose octa-acetate. Analyses showed that only in exceptional cases does the cellulose of wood remain unaltered, on the conversion of the latter into coal, up to the tertiary geological age. Other coals and lignites yielded no trace of cellulose. E. E. T.

Effect of 5*N*-Nitric Acid on Cellulose, Dextrose, Natural and Artificial Humic Acids, and Lignin. H. TROPSCH and A. SCHELLENBERG (*Ges. Abh. Kenntn. Kohle*, 1921, **6**, 257—262; from *Chem. Zentr.*, 1924, i, 562).—The action of 5*N*-nitric acid on natural and artificially prepared humic acids and on lignin is similar, nitrophenolic substances occurring amongst the products of reaction. Cellulose and dextrose behave differently. Humic acid artificially prepared from sugar is more readily attacked than natural humic acid and lignin. G. W. R.

[Esterification and Mercerisation of Cellulose.] R. O. HERZOG and G. LONDBERG (*Ber.*, 1924, **57**, [*B*], 750; cf. this vol., i, 373).—The authors' inability to obtain a monoacetate or monobenzoate of cellulose is due to the fact that further esterification occurs more rapidly in the altered layers than does monoacylation in the deeper layers. H. W.

Acetylation of Lignin. E. HEUSER and W. ACKERMANN (*Cellulosechemie*, 1924, **5**, 13—21; 30–31).—Lignin was obtained by treating resin-free wood meal with 41·2% hydrochloric acid; the product contained 13% of methoxyl and was free from residues of pentosan. This was acetylated by heating with acetic anhydride in the presence of pyridine; the acetyl value increased up to a maximum corresponding with 32·5% of combined acetic acid and then decreased on further heating owing to hydrolysis of the ester. Acetylation with acetyl chloride gave substantially identical results. Acetic anhydride alone gave inferior acetylation values as compared with those obtained in the presence of pyridine; addition of sodium acetate was still less favourable to esterification. Much more rapid esterification was effected by a mixture of acetic anhydride and nitric acid, and the same maximum limit of acetyl value was attained. On further treatment, this acetyl value decreased as before, but subsequently increased up to 42·5% owing to hydrolysis and re-acetylation of groups originally combined as methoxyl. The acetyl-lignin esters obtained were lighter in colour than the original lignin. Natural lignin existing in wood probably contains three hydroxyl groups on Klason's formula; the triacetate, $C_{41}H_{37}O_{11}(OAc)_3$, should contain 20·07% of combined acetic acid, as against 17·8% calculated from the authors' equilibrium value duly corrected. J. F. B.

Humic Acids. I. Method of Preparation. H. TROPSCH and A. SCHELLENBERG (*Ges. Abh. Kenntn. Kohle*, 1921, **6**, 191—195; from *Chem. Zentr.*, 1924, i, 600).—Rosenthal coal used for the preparation of humic acids contained 3·7% of material extractable by benzene. The ethyl alcohol extract (18·9%) contained 55% of humic substances. The humic acid used in subsequent investigations was obtained as follows. The coal was first extracted repeatedly with benzene and ethyl alcohol and the residue treated with 1% hydrochloric acid, after which it was shaken with 2*N*-sodium hydroxide. The alkaline solution was separated by filtration and centrifuging, and the humic acids were precipitated by acidifying with hydrochloric acid. The precipitate was collected and washed with water to the stage of incipient sol formation. The yield of humic acid was 60%, having the composition carbon 54·7%, hydrogen 3·0%, and ash 10·2%. G. W. R.

Humic Acids. II. Products of Alkali Fusion and Heating under Pressure. H. Tropsch and A. Schellenberg (*Ges. Abh. Kenntn. Kohle*, 1921, **6**, 196—213; from *Chem. Zentr.*, 1924, i, 600—601; cf. preceding abstract).—Humic acid (40 g.) obtained from bituminous coal was heated with potassium hydroxide (160 g.) and water (100 c.c.) at 240—300°. Humic substances were obtained in 40—50% yield. Steam distillation of the acid solution gave 3% of volatile acids, principally acetic acid together with a little formic acid, and small quantities of neutral reducing compounds. The ethereal extract contained *iso*phthalic acid, and hydroxy*iso*phthalic acid or hydroxyterephthalic acid. Oxalic acid was obtained from the residue after ether extraction. Heating humic acid under pressure with 10*N*-potassium hydroxide for 140 hours at 150° yielded 52% of humic substances soluble in alkali, containing carbon 47·9%, hydrogen 2·6%, and ash 26·7%. From these products, after acidification, acetic acid and formic acid were isolated by steam distillation, and oxalic acid by extraction with ether. *m*-Hydroxybenzoic acid and 5-hydroxy*iso*phthalic acid were also obtained. G. W. R.

Humic Acids. III. Action of Nitric Acid on Humic Acids. H. Tropsch and A. Schellenberg (*Ges. Abh. Kenntn. Kohle*, 1921, **6**, 214—234; from *Chem. Zentr.*, 1924, i, 601—602; cf. preceding abstracts).—Humic acid from coal is rapidly attacked by 5*N*-nitric acid at 60°, and by prolonged heating the material goes into solution with the exception of 4—9% of solid, brown residue. Oxalic acid and certain strongly acid substances having the character of nitrophenols are obtained. Reduction of these nitro compounds gives black, humic substances. From the ethereal extract in certain cases, 5% (calculated on the original humic acid) of *trinitrodihydroxybenzene* is obtained. It forms yellow needles, m. p. 267° (decomp.). On drying in a vacuum, water of crystallisation is lost at 80°, and the composition is then given by the formula $C_6H_3O_8N_3,0{\cdot}5H_2O$. A crystalline *tin* double salt is obtained on reduction with tin and hydrochloric acid; it forms thick, well-formed crystals. On attempting to isolate the amino compound, decomposition takes place with formation of black, humic substances. The products of reaction of humic acid with nitric acid (*d* 1·4) or with 2·5*N*-nitric acid are similar. With nitric acid (*d* 1·5), however, nitrohumic acid is obtained. The action of 5*N*-nitric on the humic acid prepared from quinol is more energetic than is the case with humic acid prepared from natural products. Oxalic acid and substances of the character of nitrophenols are obtained. Humic acid from sugar gives, with 5*N*-nitric acid at room temperature, a red, amorphous substance similar to the nitrohumic acid obtained from natural humic acid by the action of nitric acid (*d* 1·5). With nitric acid (*d* 1·5), sugar humic acid yields 20% of substances of the character of nitrophenols. G. W. R.

Humic Acids. IV. Effect of certain Reagents on Humic Acids. H. TROPSCH and A. SCHELLENBERG (*Ges. Abh. Kenntn. Kohle*, 1921, **6**, 235—247; from *Chem. Zentr.*, 1924, i, 602; cf. preceding abstracts).—Humic acid from coal yields, with 72% sulphuric acid, 87·5% of humic substances, of which 22% is soluble in alcohol; 11·4% of volatile acids, including formic acid and acetic acid, and 1·8% of an orange-red, lacquer-like substance. Hydrochloric acid reacts in a similar manner. By chlorination of humic acid suspended in *s*-tetrachloroethane, substances containing 18 to 30·8% of chlorine are obtained. Among the products of reaction of potassium chlorate and hydrochloric acid on humic acid is hexachloroethane. G. W. R.

Humic Acids. V. Dry Distillation of Humic Acid and its Alkaline Derivatives. H. TROPSCH and A. SCHELLENBERG (*Ges. Abh. Kenntn. Kohle*, 1921, **6**, 248—256; from *Chem. Zentr.*, 1924, i, 603; cf. preceding abstracts).—Dry distillation of humic acid at 525° and 0·8—5·1 mm. yields 57·5% of carbonaceous residue and gaseous products, including steam, carbon dioxide, and acetic and formic acids. Tarry substances were not obtained in the distillate. Similar products were obtained by distillation at 300° under atmospheric pressure. The humic substance obtained by heating humic acid with 10*N*-potassium hydroxide at 150° under pressure yields similar products on distillation. The substance obtained by heating humic acid with potassium hydroxide at 300° behaves differently on distillation in that it yields a certain amount of tar both at atmospheric and under reduced pressures. From the products of distillation under reduced pressure, a wax-like substance having m. p. 62° is obtained, the composition of which corresponds with a ketone, $C_{47}H_{94}O$. Distillation of humic acid with zinc dust gives, in addition to gaseous products and an aqueous distillate, a certain amount of oil having b. p. 80—130°, which by the action of nitric acid yields a heavy oil having the odour of nitrobenzene. Among the products of the distillation of humic acid with zinc dust in a current of hydrogen is an oil having the odour of pyridine and quinoline. G. W. R.

Electrolytic Reduction of Acid Oximes. M. ISHIBASHI (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 335).—γ-*iso*Nitrosovaleric acid is so easily hydrolysed in acid solution that it cannot be reduced chemically to the corresponding amine. An 84% yield of the latter is, however, obtained by electrolytic reduction, employing a current density of 2 amp. per sq. dm., a temperature of 3—5°, and a sulphuric acid concentration of less than 5%. The amine from α-*iso*nitrosopropionic acid is obtained in 95% yield with a current density of 4·5 amp. per sq. dm., a temperature of 7—10°, and an acid concentration of 8%.

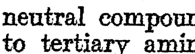
W. T. K. B.

Trialdehyde Compounds of Primary Amines. M. BERGMANN and A. MIEKELEY (*Ber.*, 1924, **57**, [*B*], 662—664; cf. Bergmann, Jacobsohn, and Schotte, this vol., i, 19).—Aliphatic aldehydes combine with primary amines to give trialdehyde compounds of the type $R\cdot CH<^{O\cdot CHR}_{O\cdot CHR}>NR'$; the property is not shared by benzaldehyde.

Triformaldehyde-ethylamine, ($R=H$; $R'=Et$), b. p. 62—64°/42 mm. (*picrate*, m. p. 75°), is prepared by the gradual addition of ethylamine to a large excess of well-cooled, aqueous formaldehyde solution (30%). *Triacetaldehyde-ethylamine* is a colourless, unstable liquid, b. p. 59—60°/15 mm. Allylamine and formaldehyde give the relatively stable *triformaldehyde-allylamine*, b. p. 38—40°/1·5 mm., together with compounds richer in aldehyde. *Triacetaldehyde-allylamine* is a colourless, exceedingly unstable liquid, b. p. 48—50°/2·5 mm. Benzaldehyde and allylamine give *benzylidene-allylamine*, b. p. 96°/12 mm., which is transformed by bromine into *benzylidene-βγ-dibromopropylamine*, m. p. 36—37°. H. W.

Action of Secondary Amines on Alkyl Chlorosulphonates. M. DÉLÉPINE and R. DEMARS (*Bull. Sci. Pharmacol.*, 1923, **30**, 577—599; from *Chem. Zentr.*, 1924, i, 415; cf. A., 1922, i, 634).—Dialkylaminosulphonic acids or their esters might be expected to be formed by the action of secondary amines on alkyl chlorosulphonates according to the equation:

$$2RR'NH+Cl\cdot SO_2\cdot OR''=RR'N\cdot SO_2\cdot OR''+NHRR',HCl.$$

Actually, however, compounds of the betaine type are obtained which may be considered as anhydrides of trialkylammonium hydroxide sulphonic acids. Their formation from dialkylaminosulphonic acids may be thus represented: $RR'N\cdot SO_2\cdot OR''\longrightarrow$  $RR'R''N<^{SO_2}_{O}$ $\longleftarrow RR'R''N(OH)\cdot SO_2\cdot OH$. They are colourless neutral compounds which hydrolyse slowly with alkalis or acids to tertiary amines and sulphuric acid, behaving in this respect like the compounds formed from sulphur dioxide and tertiary amine oxides or hydroxylamines. *Trimethylammonium hydroxide N-sulphonic anhydride*, Me_3NSO_3, from dimethylamine and methyl chlorosulphonate, forms shining needles, m. p. above 200° (decomp.). It is also formed from sulphur dioxide and trimethylamine oxide. *Dimethylethylammonium hydroxide sulphonic anhydride*, Me_2EtNSO_3, has m. p. 131—133°, and *methyldipropylammonium hydroxide sulphonic anhydride*, m. p. 120—121°. G. W. R.

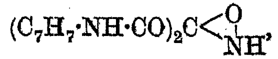
Constitution of Galegine. G. TANRET (*Bull. Soc. chim.*, 1924, [iv], **35**, 404—405; cf. A., 1914, i, 859).—One of the two open-chain structures advanced for galegine by Barger and White (this vol., i, 272) has been suggested previously by the author (Thesis, Paris, 1917). R. B.

Catalytic Decomposition of the Formic Amides. A. Mailhe (*Bull. Soc. chim.*, 1924, [iv], **35**, 363—365).—The primary amides of the formic acid series are dehydrated in contact with nickel at 400°, yielding the corresponding nitrile. The water formed in the reaction hydrolyses part of the unchanged amide to ammonia and the carboxylic acid, which in the presence of active nickel is decomposed into gaseous products and carbon.

R. B.

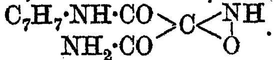
Preparation of Diethylchloroacetamide. Société Chimique des Usines du Rhône (Brit. Pat. 209706).—Diethylchloroacetyl chloride, b. p. 93°/70 mm., obtained by chlorinating diethylacetyl chloride at about 100°, is shaken with excess of ammonia or of a compound evolving ammonia (*e.g.*, ammonium carbonate). The diethylchloroacetamide produced forms white flakes, m. p. 58°, and possesses valuable soporific properties. W. T. K. B.

The Oxime of Mesoxamide (Oximinomalonamide) and some Allied Compounds. V. Structural- and Stereo-isomerism in the Methyl Ethers of the *p*-Tolyl Derivatives. A. Plowman and M. A. Whiteley (*J. Chem. Soc.*, 1924, **125**, 587—604; cf. *ibid.*, 1922, **121**, 2110).—Investigations of the ethers of alkyl- and aryl-substituted derivatives of oximinomalonamide have now been extended to the ethers of the *p*-tolyl derivatives, in which the stable yellow form appears to possess the *N*-ether structure. The yellow tautomeride of oximinomalon-*p*-toluidide, yellow scales, m. p. 170—171°, is obtained from mesox-*p*-toluidide and hydroxylamine under conditions (dilute alcoholic solution) which indicate that it possesses the *iso*oxime structure,



$$(C_7H_7\cdot NH\cdot CO)_2C<\genfrac{}{}{0pt}{}{O}{NH},$$

whereas the colourless tautomeride, thin needles, becoming yellow at 150°, m. p. 170—171°, is formed under different conditions (absolute alcoholic solution) pointing to the oxime structure, $(C_7H_7\cdot NH\cdot CO)_2C{:}NOH$. Of the two *methyl ethers* of oximino-malon-*p*-toluidide, the colourless stable *isomeride*, m. p. 171° [*hydrate*, $(C_7H_7\cdot NH\cdot CO)_2C(OH)\cdot NH\cdot OH$, m. p. 196°] from its formation from the hydrated form of mesox-*p*-toluidide and α-methylhydroxylamine must be regarded as the *O*-ether, whilst the structure of the yellow *isomeride*, m. p. 182° (decomp.), is established as the *N*-methyl ether by its hydrolysis to β-methylhydroxylamine and mesox-*p*-toluidide, and by its synthesis from the same two compounds. Further work on oximinomalonmono-*p*-tolylamide has led to the isolation of three yellow and two colourless *isomerides*. The original yellow isomeride (α), m. p. 184°, is converted into a colourless isomeride (β), m. p. 157°, by spontaneous evaporation from alcohol, and into a second colourless isomeride (β′), m. p. 175°, by the action of moist hydrogen chloride in the presence of chloroform; each of these colourless isomerides yields a corresponding yellow tautomeride (γ and γ′) when crystallised from non-hydroxylic solvents, melting at the same temperature as the parent colourless compound. On treatment with phosphorus pentachloride the β- and γ-isomerides yield *p-tolyloxamidonitrile*, $C_7H_7\cdot NH\cdot CO\cdot CN$, colourless needles, m. p. 178°, together with carbon dioxide, a reaction which indicates that they are the two structural forms of *anti-p*-tolylmesoxamideoxime, the coloured γ-isomeride possessing the *iso*oxime structure,



$$\begin{matrix} C_7H_7\cdot NH\cdot CO \\ NH_2\cdot CO \end{matrix}\!\!>C<\!\!\begin{matrix} NH \\ | \\ O \end{matrix}$$

. On treatment with phosphorus pentachloride the β′- and γ′-tautomerides undergo the normal Beckmann change and yield oxamide, carbon dioxide, and *p*-toluidine. They are therefore regarded as the structural isomerides of *syn-p*-tolylmesoxamideoxime, the true oxime structure, $NH_2\cdot CO\cdot C(:NOH)\cdot CO\cdot NH\cdot C_7H_7$, being assigned to the colourless β′-isomeride. The α-isomeride is the most stable isomeride and forms the sole product of the action of nitrosyl chloride on malonmono-*p*-toluidide. It yields the same ethers as the β- and γ-forms, and is similarly decomposed by the action of phosphorus pentachloride; it probably possesses a nitrone structure,

$$C_7H_7\cdot NH\cdot CO\cdot C(:NHO)\cdot CO\cdot NH_2.$$

The action of methyl iodide on the α-, β-, and γ-isomerides in the presence of silver oxide yields an *O-methyl ether*, colourless needles, m. p. 204°, a second colourless *ether*, flat needles, m. p. 155°, being obtained from the β′- and γ′-isomerides under similar conditions. The structure of these isomeric ethers as the *anti-* and *syn*-forms, respectively, of oximinomalonmono-*p*-toluidide,

$$C_7H_7\cdot NH\cdot CO\cdot C(:NOMe)\cdot CO\cdot NH_2,$$

is deduced from the synthesis of the isomeride, m. p. 204°, by the condensation of α-methylhydroxylamine hydrochloride in aqueous alcoholic solution with *mesoxmono-p-toluidide*,

$$C_7H_7\cdot NH\cdot CO\cdot CO\cdot CO\cdot NH_2,$$

m. p. 222° (decomp.), [*hydrate*, $C_7H_7\cdot NH\cdot CO\cdot C(OH)_2\cdot CO\cdot NH_2$, colourless plates, m. p. 222°, decomp., *phenylhydrazone hydrate*, colourless needles, yellow at 165°, m. p. 193°, *phenylhydrazone*, yellow needles, m. p. 193°], the hydrated form,

$$C_7H_7\cdot NH\cdot CO\cdot C(OH)(NH\cdot OMe)CO\cdot NH_2,$$

colourless needles, m. p. 179° (decomp.), being produced intermediately. Methylation with diazomethane converts the α-, β-, and γ-isomerides of oximinomalonmono-*p*-toluidide into an *N-methyl ether*, bright yellow, felted needles, m. p. 200° (decomp.), the β′- and γ′-isomerides yielding a second yellow *isomeride*, m. p. 150°, decomp. (*hydrate*, colourless needles). The structure of these yellow isomerides as *N*-methyl ethers of the *anti-* and *syn*-forms, respectively, of oximinomalonmono-*p*-toluidide is indicated by their hydrolysis with moist hydrogen chloride to the hydrated form of the corresponding ketone, mesoxmono-*p*-toluidide, from which a small quantity of the yellow isomeride, m. p. 200°, is formed by the action of β-methylhydroxylamine, the main product of this latter reaction being a colourless additive compound,

$$C_7H_7\cdot NH\cdot CO\cdot C(OH)(N_2Me\cdot OH)\cdot CO\cdot NH_2,$$

flat needles, m. p. 174° (decomp.), which has hitherto resisted dehydration.

Acetylation of the five isomerides of oximinomalonmono-*p*-toluidide yielded one of two colourless *acetyl* derivatives, m. p. 132° and 165°, respectively. The former is obtained from the α-oximino compound, the latter from the β′- and γ′-isomerides, the β- and γ-isomerides yielding a mixture from which only the acetyl derivative, m. p. 165°, could be isolated. On hydrolysis the latter substance yields the β′-oximino compound, whilst the compound melting at 132° yields a mixture of the α- and β-isomerides. The acetyl derivatives are accordingly regarded as acetates of the *syn-* and *anti*-type, respectively. R. B.

Thermal Decomposition of Allophanic Esters. J. Grandière (*Bull. Soc. chim.*, 1924, [iv], **35**, 187—196).—The following new esters were prepared by Béhal's method (A., 1919, ii, 301): *allophanates* of ethylpropylcarbinol (m. p. 185·5°); ethylbutylcarbinol (m. p. 187°), methyldiethylcarbinol (m. p. 152°), triethylcarbinol (m. p. 156°), methylethylpropylcarbinol (m. p. 148°), methylethylbutylcarbinol (m. p. 130°), Δ^{α}-penten-γ-ol (m. p. 155°), *o*-methyl*cyclo*hexanol (m. p. 177°), furyl alcohol (m. p. 167·5°), *o*-chlorophenol (m. p. 179°), glycol chlorohydrin (m. p. 182·5°).

On heating to 20° or 30° above the melting point most allophanic esters decompose into the alcohol and cyanuric acid, together with a small quantity of cyanic acid which reacts with the alcohol to give the corresponding urethane and allophanate. The esters of tertiary alcohols behave differently; a hydrocarbon of the ethylene series is evolved and allophanic acid probably formed as an intermediate product, but decomposes to carbamide, which immediately loses ammonia, both substances being unstable at the decomposition temperature of the ester. A certain amount of the alcohol and cyanuric acid is also formed.

The allophanates of geraniol, rhodanol, and citronellol decompose at 180—200° into carbon dioxide, ammonia, cyanuric acid, the alcohol, and a hydrocarbon, together with a brown, viscous liquid which, on hydrolysis, yields a small quantity of the corresponding alcohol. The allophanic esters of furyl and cinnamyl alcohols decompose into ammonia and carbon dioxide, leaving a resinous residue.

It is suggested that the behaviour of the allophanates of tertiary alcohols will serve for the detection of these alcohols (cf. A., 1919, ii, 301). E. E. T.

Isomeric Modifications of Methyleneaminoacetonitrile and their Biological Significance. T. B. Johnson and H. W. Rinehart (*J. Amer. Chem. Soc.*, 1924, **46**, 768—774).—Further investigation of the methyleneaminoacetonitriles, m. p. 129° and 86°, obtained by Klages (A., 1903, i, 469) has shown that they are structural isomerides having the formula $C_9H_{12}N_6$. The two compounds have different crystalline forms, behave differently on hydrolysis, and the one cannot be transformed into the other. The compound, m. p. 129°, for which the designation α-hydroformamine cyanide is proposed, forms orthorhombic crystals; β-hydroformamine cyanide, m. p. 86°, forms monoclinic crystals. C. J. S.

Deaminisation. III. Evidence of the Existence of Aliphatic Diazonium Salts from the Formation of Chloro-oximino Compounds. G. S. SKINNER (*J. Amer. Chem. Soc.*, 1924, **46**, 731—740).—The formation of ethyl chloro-oximinoacetate from the hydrochloride of ethyl aminoacetate and nitrous acid at low temperatures is presented as evidence of the existence of an aliphatic diazonium salt. It is believed to be produced according to the scheme: $NH_2{\cdot}CH_2{\cdot}CO_2Et,HCl \xrightarrow{+HNO_2} Cl{\cdot}N_2{\cdot}CH_2{\cdot}CO_2Et \xrightarrow{+HNO_2} Cl{\cdot}N_2{\cdot}CH(N{:}O){\cdot}CO_2Et \longrightarrow OH{\cdot}N{:}CCl{\cdot}CO_2Et$. A modifie dmethod is given for the preparation of ethyl and *n*-butyl diazoacetates. By the action of nitrous anhydride and of nitrosyl chloride on the ethyl diazoacetate a nitrile oxide, $C(\vdots N{:}O){\cdot}CO_2Et$, b. p. 132—133°/3 mm., d_4^{20} 1·2780, d_4^{25} 1·2726, was obtained which is unimolecular in benzene, bimolecular in ethylene dibromide, and intermediate in nitrobenzene; it has also been obtained from ethyl chloroaminoacetate and sodium carbonate. The decomposition of ethyl and *n*-butyl aminoacetates by nitrous acid in the presence of hydrochloric acid leads to the formation of the corresponding chloroacetates. Ethyl pyrazolinetricarboxylate, m. p. 98°, has been obtained by treating ethyl aminoacetate hydrochloride with nitrous acid in a manner described in the original and preserving the resulting liquid, b. p. 5—40°/4—5 mm., for several months. The preparation of *chloro-oximinoethane*, $CCl({:}N{\cdot}OH){\cdot}Me$, m. p. 84—85°, by the action of nitrous acid on ethylamine is described.

C. J. S.

Reactions of certain Aromatic and Aliphatic Derivatives. A. ANGELI (*Atti R. Accad. Lincei*, 1924, [v], **33**, 109—116).—The author quotes fresh data confirming his rule concerning the analogy of behaviour exhibited between two groups united directly and the same groups occupying ortho- or para-positions in one and the same aromatic nucleus (cf. A., 1923, i, 1003).

With reference to the mobility which the alkoxy groups of an aromatic nucleus impress on the halogen atoms of side chains in the ortho- or para-position to such groups, Werner and Goldschmiedt have shown that, whilst the group $CHPhCl$(or Br)· resists the action of boiling alcohol, the analogous ortho- or para-substituted groups, $OMe{\cdot}C_6H_4{\cdot}CHCl$(or Br)· and $CH_2O_2{:}C_6H_3{\cdot}CHCl{\cdot}$, are readily converted into $OMe{\cdot}C_6H_4{\cdot}CH(OEt){\cdot}$ and $CH_2O_2{:}C_6H_3{\cdot}CH(OEt){\cdot}$. Similarly, simple heating with alcohol produces the changes $OMe{\cdot}CH_2Cl \longrightarrow OMe{\cdot}CH_2{\cdot}OEt$(or Me). Such behaviour is limited to the halogen atom united to the carbon contiguous to the aromatic ring, halogens in other positions keeping their places; thus,

$$OMe{\cdot}C_6H_4{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2H + Et{\cdot}OH \longrightarrow OMe{\cdot}C_6H_4{\cdot}CH(OEt){\cdot}CHBr{\cdot}CO_2H.$$

The same holds with aliphatic compounds containing a halogen atom at a distance from the carbon atom united to the alkoxyl; thus, the compounds $OMe{\cdot}CH_2{\cdot}CH_2Cl(I)$, $OEt{\cdot}CH_2{\cdot}CH_2I$, $OMe{\cdot}CH_2{\cdot}CBr(NO_2)_2$, and $O(CH_2{\cdot}CH_2I)_2$ are so stable that some of them resist the actions of sodium, zinc, sodium acetate, and silver acetate, whereas the compounds $O[CH_2Cl(or\ Br)]_2$ are so unstable that they decompose in moist air.

This varying behaviour of halogen atoms according to their position furnishes explanations for many reactions. The ready elimination of the halogen is regarded by Zincke and Werner as due to the formation of an intermediate oxonium or quinonic compound, thus, $OMe\cdot C_6H_4\cdot CHRBr \longrightarrow BrMe{-}O{:}C_6H_4{:}CHR$, or $OH\cdot C_6H_4\cdot CH_2Br \longrightarrow O{:}C_6H_4\cdot H(CH_2Br) \longrightarrow OH\cdot C_6H_4\cdot CH_2\cdot OEt$; an intermediate oxonium compound is probably formed in the case of the aliphatic derivatives: $OMe\cdot CH_2Br \longrightarrow BrMe{-}O{:}CH_2$. [Cf. Hoering, A., 1904, i, 577.]

Certain groups, such as the nitro and cyano residues, enhance the activity of other groups in the para-position in an aromatic nucleus. Thus, the nitrosoamine, $NPhMe\cdot NO$, exhibits indifferent behaviour and gives up the nitroso residue only with difficulty, whereas its *p*-nitro derivative, $NO_2\cdot C_6H_4\cdot NMe\cdot NO$, immediately yields diazomethane when treated with cold sodium hydroxide. Further, alkyl ethers of phenols yield their alkyl groups only as the result of energetic reactions, but if a nitroso- or an azo-group is introduced in the ortho position to the alkoxyl, the alkyl residue is easily removed with formation of the corresponding phenols: $Ph\cdot N_2\cdot C_6H_4\cdot OMe \longrightarrow Ph\cdot N_2\cdot C_6H_4\cdot OH$, and $NO\cdot C_6H_4\cdot OMe \longrightarrow NO\cdot C_6H_4\cdot OH$. Recently, Borsche and Exss (this vol., i, 218) have shown that the azo group increases the activity of halogen atoms in the ortho- or para-position, although its effect is less than that of other negative groups, such as the nitro, cyano, carbethoxy groups, etc.

In addition to the numerous examples, given earlier, of the migration of an oxygen atom from nitrogen to carbon, in aliphatic as well as in aromatic compounds, mention is made of the following, which take place under the influence of an alkali: the conversion of nitrocoumarone into an oxime, $C_6H_4<\begin{smallmatrix}CH\\O\end{smallmatrix}>C\cdot NO_2 \longrightarrow$ $C_6H_4<\begin{smallmatrix}CO\\O\end{smallmatrix}>C{:}NOH$, and the formation of an amide, $N_3\cdot C_6H_4\cdot CO\cdot NH_2$, from the *o*-azide, $N_3\cdot C_6H_4\cdot CH{:}NOH$; the latter change is the only example of such a transposition taking place in an alkaline medium.

T. H. P.

Low-temperature Tar obtained from the Zeche Fürst Hardenberg Coal and, in particular, the Content of Benzene, Phenol, and Acetone. Reply to Broche. F. Schütz, W. Buschmann, and H. Wissebach (*Ber.*, 1924, **57**, [*B*], 619—622; cf. A., 1923, i, 907).—The conflicting results obtained by Broche are due to the fact that the authors dealt with the composition of the so-called "tar benzines" (*i.e.*, the light oils obtained by dehydrating primary tar), whereas Broche mixed the "tar benzines" and the "gas benzines" together before examination. The authors confirm their previous results (cf. A., 1923, i, 195, 452) regarding the content of benzene, phenol, and acetone. H. Lange obtained 30 kg. of pure acetone on working up 120 cubic metres of tar-water; the authors do not accept Broche's suggestion that their "abnormal" results were due to overheating of the retorts. F. A. M.

Remarks on F. Fischer's Paper, "The Relation between Low-temperature Tar, Coke-oven Tar, and Petroleum." F. SCHÜTZ (*Ber.*, 1924, 57, [*B*], 623—627; cf. A., 1923, i, 889).—Facts are quoted, such as the percentage of aromatic hydrocarbons, specific gravities, etc., to prove that Fischer's view as to the similarity between crude petroleum and low-temperature tar cannot be maintained. On the contrary, the products obtained from the low-temperature carbonisation of coal must be regarded as new types of products which cannot be compared with the great majority of natural petroleums but are of great technical importance. [Cf. also preceding abstract.] F. A. M.

Japanese Petroleum. II. S. KOMATSU and N. TANAKA (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 143—146; cf. this vol., i, 502).—Petroleum from Nishiyama, Echigo, contains benzene and *n*-hexane.

Hydrogenation of Aromatic Compounds with the Aid of Platinum. VII. Decahydronaphthalene prepared using Platinum Black. R. WILLSTÄTTER and F. SEITZ (*Ber.*, 1924, 57, [*B*], 683—684; cf. A., 1923, i, 771).—According to Hückel (this vol., i, 31), all preparations of decahydronaphthalene are mixtures of the *cis*- and *trans*-forms, the product obtained by the use of platinum black containing about 90% of the *cis*- and 10% of the *trans*-form. The authors have examined various preparations made with the aid of platinum and found all to have the constants (b. p. 193—193·5° corr.; d_4^{20} 0·8938—0·8942; n_D^{20} 1·4796) of the pure *cis*-form, nor could any trace of the *trans*-form be obtained on fractional distillation. Reduction of naphthalene with nickel and hydrogen at 160—162°, however, yielded chiefly the *trans*-form, d_4^{20} 0·8784; n_D^{20} 1·4729. F. A. M.

Preparation of Tetralin [Tetrahydronaphthalene]. H. INOUE (*J. Chem. Ind. Japan*, 1923, 26, 1316—1329).—For the hydrogenation of naphthalene, electrolytic hydrogen was used, and the nickel catalyst was prepared by electrolysing a 5—10% solution of sodium phthalate containing a slight excess of phthalic acid at 17—25°, using a nickel anode; the nickel hydroxide precipitated in the neighbourhood of the cathode is more active than that obtained by any other process. It is converted into oxide and then to metal at 310—320°. Purified naphthalene containing only 0·04% of sulphur was used and the hydrogenation was conducted in a specially designed autoclave of 7 litres capacity at 30 atm. pressure. The tetralin obtained had, after distillation, *d* 0·970. Decalin was prepared from tetralin by the same process. K. K.

Lely's Benzene Theory. J. D. VAN ROON (*Chem. Weekblad*, 1924, 21, 174).—A reply to Lely's response (this vol., i, 380) to the author's criticism of the theory. S. I. L.

Electrochemical Oxidation of Aromatic Hydrocarbons. F. FICHTER (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 75—95).—A general theoretical discussion of the electrolytic oxidation of benzene derivatives, illustrated mainly by the results of the author and his collaborators. Benzene is oxidised first to phenol, then to quinol and pyrocatechol, eventually to quinone, and is finally completely disrupted. The oxidation process is governed by the following factors: (1) concentration, (2) current density, (3) nature of anode, (4) influence of cathode if no diaphragm be used, (5) nature of the electrolyte, (6) secondary reactions, *i.e.* use of a solution of a salt of a metal having a variable valency, (7) superimposition of alternating on direct current.

When phenols are oxidised, the tendency is for *p*-quinones to be formed; thus anisole gives benzoquinone, *m*-tolyl methyl ether yields toluquinone, and *m*-xylenol *p*-xyloquinone. When phenol itself is appropriately oxidised there are formed, besides the usual products, certain hydroxydiphenyls and diphenyl ethers (Fichter and Brunner, A., 1916, i, 644; Fichter and Ackermann, A., 1919, i, 586). Recent investigation, the results of which remain unpublished, has shown that guaiacol, *p*-tolyl methyl ether, and *m*-xylenol similarly yield 4 : 4′-dihydroxy-3 : 3′-dimethoxydiphenyl, 2-hydroxy-2′-methoxy-4 : 4′-dimethyldiphenyl, and 2 : 2′-dihydroxy-3 : 5 : 3′ : 5′-tetramethyldiphenyl respectively. W. A. S.

Action of Sodium Sulphite on some Trinitro Compounds and on Tetranitromethane. Purification of Tolite [2 : 4 : 6-Trinitrotoluene]. H. MURAOUR (*Bull. Soc. chim.*, 1924, [iv], **35**, 367—379; cf. A., 1922, i, 443, 1006).—Dilute solutions of sodium sulphite (3 to 5%) dissolve 2 : 3 : 4-trinitrotoluene (β) and 2 : 4 : 5-trinitrotoluene (γ) in the cold, giving colourless solutions of the corresponding sodium dinitrosulphonates, one of the adjacent ortho-nitro groups being replaced. Thus 2 : 4 : 5-trinitrotoluene is converted into sodium 2 : 4-dinitrotoluene-5-sulphonate. Symmetrical trinitrotoluene, however, only reacts slightly with dilute sodium sulphite, forming an additive product which is only stable in concentrated solutions of the sulphite and from which, on dilution, the greater part of the trinitrotoluene is precipitated. Trinitrobenzene dissolves in cold dilute sodium sulphite giving an intense red solution, from which the trinitrobenzene is precipitated unchanged on acidifying. *s*-Trinitro-*m*-xylene and trinitromesitylene do not react with aqueous sodium sulphite. Tetranitromethane reacts readily; the reaction appears to proceed in two stages, the sodium trinitromethanesulphonate first formed being subsequently hydrolysed to the sodium salt of trinitromethane.

The purification of crude commercial trinitrotoluene by the sodium sulphite process is discussed, and the application of the process to the determination of the unsymmetrical trinitrotoluenes in crude trinitrotoluene is described.

The reaction has also been utilised for the separation and approximate determination of the trinitroxylenes, the trinitro-derivatives of *o*- and *p*-xylene reacting with dilute sodium sulphite, whilst trinitro-*m*-xylene does not. [Cf. *B.*, 1924, 451.] R. B.

Sulphonation of *p*-Cymene. M. PHILLIPS (*J. Amer. Chem. Soc.*, 1924, **46**, 686—694).—The proportions of the isomeric monosulphonic acids produced by sulphonation of *p*-cymene have been investigated using a method based on the melting-point curves of the corresponding sulphonamides. The proportion of sulphuric acid used has less effect than temperature. The best yield of the β-acid (*p*-cymene-3-sulphonic acid) is obtained using 1 part of *p*-cymene to 3 parts of sulphuric acid, sulphonating for 4 hours at 100°. Sulphonation at lower temperatures favours formation of the 2-isomeride; thus 15·6% of the 3-sulphonic acid is formed at 100° and 2·5% at 0° (using fuming sulphuric acid containing 20% of anhydride). No disulphonic acid appears to be formed at or below 50°, but increasing amounts are produced at higher temperatures. The proportion of *p*-cymene-2-sulphonic acid is somewhat increased by addition of copper or mercuric sulphate.

C. J. S.

Synthesis of Higher Homologues of *m*-Methylethylbenzene. A. MAILHE (*Bull. Soc. chim.*, 1924, [iv], **35**, 365—367).—By the action of acid chlorides on *m*-methylethylbenzene in carbon disulphide solution in the presence of aluminium chloride, followed by hydrogenation of the ketone first formed in the presence of nickel according to Darzens' method (A., 1905, i, 66), a number of higher homologues of *m*-methylethylbenzene have been obtained. The new alkyl group enters the benzene ring in the 6-position. 2-*Methyl-4-ethylacetophenone* has b. p. 239—240° (*semicarbazone*, m. p. 185°), 1-*methyl-3* : 6-*diethylbenzene*, b. p. 205—207°; 2-*methyl-4-ethylphenyl ethyl ketone*, b. p. 250—252°; 1-*methyl-3-ethyl-6-propylbenzene*, b. p. 213—215°, d_4^{11} 0·8831; 2-*methyl-4-ethylphenyl* iso*propyl ketone*, m. p. 132°, b. p. 258—259°, d_4^{11} 0·9557; 1-*methyl-3-ethyl-6-*iso*butylbenzene*, b. p. 228—229°, d_4^{11} 0·8863; 2-*methyl-4-ethylphenyl propyl ketone*, b. p. 265—266°; 1-*methyl-3-ethyl-6-butylbenzene*, b. p. 236—237°, d^{11} 0·6882(?); 2-*methyl-4-ethylphenyl* iso*butyl ketone*, b. p. 274°; 1-*methyl-3-ethyl-6-*iso*amylbenzene*, b. p. 245—246°, d^{11} 0·8801. By the action of benzoyl chloride on *m*-methylethylbenzene in the presence of aluminium chloride 2-*methyl-4-ethylbenzophenone*, b. p. 318—320°, was obtained, which on hydrogenation was converted into 2-*methyl-4-ethyldiphenylmethane*, b. p. 298—300°, d^{11} 1·0141. R. B.

Alkylation of Primary Amines with Aluminium Alkoxides to give Secondary Amines Free from Tertiary Amines. W. A. LAZIER and H. ADKINS (*J. Amer. Chem. Soc.*, 1924, **46**, 741—746).—Both aromatic and aliphatic primary amines may be alkylated by heating with aluminium alkoxide in sealed tubes at 250—350°. Aniline with aluminium ethoxide yielded a colourless reaction product containing 94% of ethylaniline and 6% of aniline. Other secondary amines were prepared in good yield by alkylating aniline, *p*-toluidine, and *n*-amylamine, but the optimum conditions have not yet been ascertained. The yields obtained, using acetanilide in place of aniline, were considerably lower. These results do not support Nef's dissociation hypothesis (A., 1901, i, 626), by which he explained the mechanism of alkylation.

C. J. S.

Highly Chlorinated Hydroaromatic Products containing Nitrogen. DURAND und HUGUENIN A.-G. (Brit. Pat. 198676).—Amines containing negative substituents are chlorinated, in the absence of moisture, without previously protecting the amino group by salt formation, as is necessary in the case of the unsubstituted amines (cf. Brit. Pat. 193843). For example, chlorine is introduced into an ice-cooled solution of 20 g. of 2 : 5-dichloroaniline in 600 c.c. of chlorobenzene. The paste initially formed having become fluid, the mixture is heated at about 100°, filtered, and the chlorobenzene distilled under diminished pressure. A crystalline compound (containing eight chlorine atoms) separates, which crystallises from light petroleum in colourless laminæ, m. p. 125°.

W. T. K. B.

Nitration of *p*-Bromoacetanilide. R. H. GRIFFITH (*J. Chem. Soc.*, 1924, **125**, 940—941).—The nitration of *p*-bromoacetanilide at 10° with excess of nitric acid and sulphuric acid yields 2 : 4-dibromo-6-nitroacetanilide, m. p. 215°, 4-bromo-2 : 6-dinitroacetanilide, and 4-bromo-2-nitroacetanilide. 2 : 4-Dibromoacetanilide nitrated with excess of fuming nitric acid yields 2 : 4-dibromo-6-nitroacetanilide, which is hydrolysed to 2 : 4-dibromo-6-nitroaniline, m. p. 128°, with alcoholic hydrochloric acid. Nitration in the presence of sulphuric acid yields 2 : 4-dibromo-5-nitroacetanilide, m. p. 172°. 4-Bromo-2 : 6-dinitroaniline melts at 162°.

R. B.

Electrolytic Preparation of Metanilic Acid and its Commercial Possibilities. A. K. DOOLITTLE (*Trans. Amer. Electrochem. Soc.*, 1924, 45, 43—62).—In only one particular is the electrolytic reduction of *m*-nitrobenzenesulphonic acid likely to be more advantageous than the usual iron reduction, and that is that the former process might be made continuous. The author has therefore investigated the electrolytic method, using lead electrodes and 10% sulphuric acid as electrolyte. To the cathode solution, contained in a porous vessel, pure calcium *m*-nitrobenzenesulphonate was added. Reduction did not take place at 24°. The best results were obtained at 70°, with a bright lead cathode, current density 0·585 amp. per sq. dm., and cathode solution 1%. The yield was 67% of theory and current efficiency 64%. [Cf. *B.*, 1924, 288.]

W. A. S.

Crystallographic Investigation of *p*-ββ-Dimethylpropylbenzenesulphanilide and Benzyltrimethylsilicane-*p*-sulphanilide. N. ZENZÉN (*Arkiv Kem., Min., Geol.*, 1923, **8**, No. 34, 1—10).—*p*-ββ-Dimethylpropylbenzenesulphanilide,

$$CMe_3\cdot CH_2\cdot C_6H_4\cdot SO_2\cdot NHPh$$

(cf. Bygdén, A., 1920, i, 478), crystallises in holohedral monoclinic crystals, $a:b:c=0\cdot6869:1:0\cdot7536$, $\beta=113°\ 17'$, and benzyltrimethylsilicane-*p*-sulphanilide, $SiMe_3\cdot CH_2\cdot C_6H_4\cdot SO_2\cdot NHPh$ (cf. Bygdén, A., 1918, i, 134), also in holohedral monoclinic crystals, $a:b:c=0\cdot6973:1:0\cdot7698$, $\beta=113°\ 38'$. True mixed crystals of these two compounds are formed. The axial angle usually has appreciably different values at the two sides of a mixed crystal, probably on account of its zonal structure. T. H. P.

Decomposition of Quaternary Ammonium Hydroxides. J. v. Braun and R. S. Cahn (*Annalen*, 1924, **436**, 262—273; cf. A., 1911, i, 610).—The decomposition of β-phenylethyltrimethylammonium hydroxide giving a quantitative yield of styrene and a tertiary base has been applied to the synthesis of tertiary bases previously difficult to obtain. By the action of β-phenylethylamine on ethyl αα′-dibromoadipate in chloroform solution are obtained *ethyl* β-*phenylethylpyrrolidine*-2 : 5-*dicarboxylate*, oil, b. p. 212—214°/14 mm. (*chloroplatinate*, decomp. 160—161°), and ethyl αα′-di(β-phenylethylamino)adipate,

$$[CO_2Et\cdot CH(NH\cdot CH_2\cdot CH_2Ph)CH_2\cdot]_2,$$

a thick oil; the free acid, $C_{22}H_{28}O_4N_2$, forms long, colourless needles, m. p. 118°. 1-β-*Phenylethylpyrrolidine*-2 : 5-*dicarboxylic acid*, colourless crystals, decomp. 215° (*hydrochloride*, m. p. 177—178°), on dry distillation gives 1-β-phenylethylpyrrolidine, a mobile oil, b. p. 138—139°/21 mm. (*picrate*, m. p. 139—140°, *methiodide*, m. p. 143°). The methiodide on treatment with silver oxide and distillation of the quaternary ammonium hydroxide gives 60% of the theoretical yield of styrene and 1-methylpyrrolidine, b. p. 78°. Reduction of ethyl 1-β-phenylethylpyrrolidine-2 : 5-dicarboxylate with sodium and alcohol yields 1-β-*phenylethyl*-2 : 5-*dihydroxymethylpyrrolidine*, a viscous, colourless oil, b. p. 225°/13 mm. (*hydrochloride*, m. p. 127—129°, *picrate*, m. p. 108—111°, *methiodide*, oily), but the yield is small and no attempt was made to convert it into the corresponding 1-methylpyrrolidine.

β-Phenylethyldimethylamine reacts readily with *o*-xylylene bromide (for the preparation of which a new method from *o*-toluidine is described), in chloroform solution, yielding the *diquaternary bromide*, $C_{28}H_{38}N_2Br_2$, colourless crystals, m. p. 206°, which on treatment with silver oxide and distillation gives 65% of the theoretical yield of styrene and 60% of tetramethyl-*o*-xylylenediamine, $C_6H_4(CH_2\cdot NMe_2)_2$, colourless oil, b. p. 105—106°/14 mm. [*picrate*, m. p. 187—188°, *methiodide*, m. p. 219° (decomp.)].

β-Phenylethyldimethylamine and αε-dibromopentane react readily at water-bath temperature, giving the *diquaternary bromide*, $CH_2(CH_2\cdot CH_2\cdot NMe_2Br\cdot CH_2\cdot CH_2Ph)_2$, m. p. 121°, which on conversion into the hydroxide and distillation gives 60% of the theoretical yield of styrene and 25% of tetramethylpentamethylenediamine.

R. B.

Tenacity of Organic Residues. II. J. v. Braun and H. Engel (*Annalen*, 1924, **436**, 299—320; cf. A., 1923, i, 1193).—Further experiments have been undertaken to test the relative firmness of attachment of groups of the benzyl and allyl type to nitrogen and to halogen. By decomposition of appropriate tertiary bases with cyanogen bromide, it is shown that the introduction of the groups Me, Et, Ph, respectively, into the para-position in the benzyl radical diminishes in the order named the firmness with which the substituted benzyl group is attached to nitrogen. A similar result was obtained from experiments in the allyl series with the radicals allyl, crotonyl, and cinnamyl. The affinity of the radicals for nitrogen (and also for carbon) accordingly stands in the order $Me < Et < Ph$, and the same order holds in regard to chlorine. These results are at variance with those of Meerwein (A., 1920, i, 2) and Skraup (A., 1919, i, 598; 1922, i, 574), but the order $Ph < p\text{-}C_6H_4Me\cdot < p\text{-}C_6H_4Et\cdot < p\text{-}C_6H_4Ph\cdot$ is in accordance with Skraup's observations and those of Schlenk on the dissociation of hexa-arylethanes. A comparison of the allyl and benzyl series shows that in regard to nitrogen the radicals can be arranged in the following order of diminishing affinity: $CH_2Ph–$, $CH_2{:}CH\cdot CH_2–$, $CHMe{:}CH\cdot CH_2–$, $CHPh{:}CH\cdot CH_2–$, $p\text{-}C_6H_4Me\cdot CH_2–$, $p\text{-}C_6H_4Et\cdot CH_2–$, $p\text{-}C_6H_4Ph\cdot CH_2–$, methylation of the benzyl residue in the para-position decreasing the firmness of its attachment to nitrogen more than phenylation of the allyl residue. Similar results were obtained by studying the reaction of benzyl, *p*-methylbenzyl, *p*-ethylbenzyl, and *p*-phenylbenzyl chlorides with sodium ethoxide.

p-*Ethylbenzyl alcohol*, b. p. 115—117°/9 mm., was obtained by the action of potassium hydroxide on the corresponding aldehyde, prepared by Gattermann's method (A., 1897, i, 519), and with hydrochloric acid was converted into p-*ethylbenzyl chloride*, b. p. 81—82°/11 mm. p-*Phenylbenzyl chloride*, m. p. 68°, is similarly prepared through p-*phenylbenzyl alcohol*, m. p. 101—102°, b. p. 183—184°/11 mm., from *p*-phenylbenzaldehyde (obtained from diphenyl by Gattermann's method), or alternatively from *p*-phenylbenzonitrile by catalytic reduction to p-*phenylbenzylamine*, colourless crystals, m. p. 127—128° (*hydrochloride*, sparingly soluble, m. p. 282°; *picrate*, m. p. 205°; *acetyl* derivative, m. p. 180°; *benzoyl* derivative, m. p. 162°; *phenylthiocarbamide*, m. p. 150°; *methiodide*, m. p. 221°), and conversion of the amide into the alcohol by the diazo reaction. The secondary base, *di*-p-*phenylbenzylamine*, m. p. 132° (*hydrochloride*, m. p. above 300°, *nitroso* compound, m. p. 170°), is also formed in the reduction.

Benzylmethylamine (obtained by catalytic reduction of benzylidenemethylamine with nickel at 100°) with *p*-methylbenzyl chloride yields *benzyl*-p-*methylbenzylmethylamine*, colourless liquid, b. p. 160°/11 mm. (*methiodide*, m. p. 190°), which is converted by cyanogen bromide into a quaternary *salt*, probably *benzyldi*-p-*methylbenzylmethylammonium bromide*, m. p. 184°, p-*methylbenzyltrimethylammonium bromide*, m. p. 170—175°, and benzylmethylcyanamide, b. p. 139—140°/12 mm. In a similar manner *benzyl*-p-*phenylbenzylmethylamine*, m. p. 44°, b. p. 190—192° (*hydrochloride*, m. p. 187°; *picrate*, m. p. 146°; *methiodide*, m. p. 162°), is obtained and transformed by cyanogen bromide into an oily quaternary salt, *p*-phenylbenzyltrimethylammonium bromide, m. p. 200°, and benzylmethylcyanamide.

p-*Methylbenzylmethylamine*, b. p. 83°/11 mm. (*hydrochloride*, m. p. 174°; *picrate*, m. p. 145°), was obtained by reduction of the Schiff's base from *p*-tolualdehyde and methylamine with sodium and alcohol. With *p*-ethylbenzyl chloride this yields the tertiary base, p-*methylbenzyl*-p-*ethylbenzylmethylamine*, b. p. 181°/9 mm., which on treatment with cyanogen bromide yields the quaternary salt, $C_6H_4Me\cdot CH_2\cdot NMe(CH_2\cdot C_6H_4Et)_2Br$, m. p. 168°; *p*-ethylbenzyltrimethylammonium bromide (chloroplatinate, m. p. 216°), and *p*-methylbenzylmethylcyanamide. p-*Methylbenzyl*-p-*phenylbenzylmethylamine*, b. p. 253—255°/13 mm., was similarly obtained from *p*-phenylbenzyl chloride, and this base by treatment with cyanogen bromide yields an oily quaternary salt, *p*-phenylbenzyltrimethylammonium bromide, m. p. 200°, and a substance, m. p. 70°, containing bromine, probably formed by the action of cyanogen bromide on the primarily formed *p*-methylbenzylmethylcyanamide. In a similar way p-*methylbenzylmethylbutenylamine*,

$$C_6H_4Me\cdot CH_2\cdot NMe\cdot CH_2\cdot CH{:}CHMe,$$

b. p. 116—118°/11 mm., is obtained by the action of crotonyl bromide on p-*methylbenzylmethylamine*, and this base is transformed by cyanogen bromide into an oily quaternary compound, *p*-methylbenzyltrimethylammonium bromide (m. p. 184°), and *methylcrotonylcyanamide*, $CHMe{:}CH\cdot CH_2\cdot NMe\cdot CN$, b. p. 92—93°/55 mm.

p-*Methylbenzylcinnamylmethylamine*, b. p. 218—220°/12 mm., is decomposed by cyanogen bromide with production of an oily quaternary salt, *p*-methylbenzyltrimethylammonium bromide (m. p. 194°), and cinnamylmethylcyanamide.

p-*Ethylbenzylmethylamine*, b. p. 105°/10 mm., obtained by the action of *p*-ethylbenzyl chloride on methylamine, reacts with *p*-phenylbenzyl chloride, yielding p-*phenylbenzyl*-p-*ethylbenzylmethylamine*, b. p. 255—257°/11 mm. (*hydrochloride*, m. p. 205°), which on decomposition with cyanogen bromide gives an oily quaternary salt, *p*-phenylbenzyltrimethylammonium bromide, and *p*-ethylbenzylmethylcyanamide.

p-*Phenylbenzylmethylamine*, b. p. 173—174°/11 mm., was obtained by condensing *p*-phenylbenzaldehyde with methylamine and reducing the Schiff's base (m. p. 51°) with sodium. With cinnamyl bromide, it yields an oily quaternary compound which on distillation in a vacuum yields a tertiary *base*, $C_{23}H_{23}N$ (*hydrochloride*, m. p. 224°), which is converted by cyanogen bromide into an oily quaternary salt, *p*-phenylbenzyltrimethylammonium bromide (m. p. 198°), and cinnamylmethylcyanamide.

Cinnamylmethylamine is a mobile liquid, b. p. 110—112°/12 mm. With allyl bromide it yields *cinnamylmethylallylamine*, $CHPh{:}CH\cdot CH_2\cdot NMe\cdot CH_2\cdot CH{:}CH_2$, b. p. 166—168°/11 mm., which on decomposition with cyanogen bromide yields an oily quaternary compound (*chloroplatinate*, $C_{44}H_{52}N_2\cdot Cl_6Pt$, m. p. 85°), cinnamyltrimethylammonium bromide (m. p. 165°), and *methylallylcyanamide*, $CH_2{:}CH\cdot CH_2\cdot NMe\cdot CN$. Similarly from cinnamylmethylamine and crotonyl chloride is obtained *cinnamylmethylcrotonylamine*, b. p. 180—182°/10 mm., from which the quaternary salt, $(CHPh{:}CH\cdot CH_2)_2NMe(CH_2\cdot CH{:}CHMe)Br$, m. p. 79°, cinnamyl bromide, and methylcrotonylcyanamide are formed on treatment with cyanogen bromide. R. B.

Catalytic Reduction of Phenol and α-Naphthol under High Pressure. H. Inoue (*J. Chem. Ind. Japan*, 1923, **26**, 1330—1334; cf. this vol., p. 628).—By the same method as that used in the catalytic preparation of tetralin, phenol was reduced at about 200° to *cyclo*hexanol (b. p. 135°, d^{20} 0·9547, n_D^{20} 1·4650), and α-naphthol to a mixture of tetralin (46·6%), *ar*-tetrahydro-α-naphthol (40·9%), and α-ketotetrahydronaphthalene (12·5%). K. K.

Esterification of *cyclo*Hexanol and some of its Homologues. (Mlle.) G. Cauquil (*Compt. rend.*, 1924, **178**, 1538—1540; cf. this vol., i, 280).—On heating 2-, 3-, and 4-methyl*cyclo*hexanol with acetic acid, 49·8%, 53·1%, and 54·1%, respectively, of the three alcohols has undergone esterification at equilibrium, showing a decrease of 5·8, 2·5, and 1·5%, compared with *cyclo*hexanol. For 3 : 4-dimethyl*cyclo*hexanol the corresponding decrease is 8·1 and for 2-ethyl*cyclo*hexanol, 6·4%. J. W. B.

Preparation of Stereoisomerides in the Disubstituted *cyclo*Hexanol Series. M. Godchot and P. Bedos (*Compt. rend.*, 1924, **178**, 1184—1186).—The action of hypochlorous acid on Δ^3-methyl*cyclo*hexene results in the formation of a mixture of two isomerides of *4-chloro-1-methyl*cyclo*hexan-3-ol.* These were separated by repeated fractionations, and the two fractions were converted by the Grignard reaction into two *1 : 4-dimethyl*cyclo*hexan-2-ols*, yielding *allophanates* of m. p. 158° and 125°, respectively. The alcohols on regeneration from these esters were colourless liquids, b. p. 175°/760 mm., d^{17} 0·9066, n_D^{17} 1·4521, and b. p. 177°/760 mm., d^{17} 0·9079, n_D^{17} 1·4544, respectively. On oxidation with chromic acid, both alcohols give *1 : 4-dimethyl*cyclo*hexan-2-one*, b. p. 171—172°; *semicarbazone*, m. p. 122°. H. J. E.

Auto-oxidation and Anti-oxygens. Catalytic Properties of Iodophenols. C. Moureu, C. Dufraisse, and J. P. des Touches (*Compt. rend.*, 1924, **178**, 1497—1501; cf. A., 1922, i, 250; 1923, ii, 308).—The inhibiting action on the auto-oxidation of acraldehyde of substances containing both a phenolic group and iodine in the same molecule has been studied. Within the limits of experimental error, neither exaltation nor diminution in the activity of the phenol group occurs. Thus *o*-iodophenol exhibits a very slight diminution in activity compared with phenol itself. The very slight activity of iodobenzene shows that iodine in the nucleus has very little effect; but the introduction of a second phenolic group in the *o*-position (pyrocatechol) increases the activity coefficient 200 times. The activities of 2 : 6- and 3 : 4-di-iodophenol, and 2 : 4 : 6-tri-iodophenol are only slightly greater than that of phenol itself, and in equal molecular concentration 2 : 6-di-iodoquinol has the same activity as quinol. The dimethyl ether of monoiodoquinol has the same activity as quinol dimethyl ether, each exhibiting an initial retarding effect followed by a distinct acceleration of the auto-oxidation. J. W. B.

Nitration. II. Mononitration of Phenol. F. Arnall (*J. Chem. Soc.*, 1924, **125**, 811—816; cf. *ibid.*, 1923, **123**, 3111).—Nitration of phenol in an organic solvent gives much better results than in aqueous solution, but the velocity of nitration depends on the nature of the solvent. At 10°, reaction in acetic anhydride containing 10% of nitric acid is apparently instantaneous. In acetone, nitration with 10% nitric acid proceeds to the extent of 80% in 3 hours; in ether, 68% in 12 hours; in alcohol (2 parts) and acetic acid (1 part), 75% in 48 hours; in absolute alcohol, 55% in 48 hours. The relative proportions of the isomerides are independent of the solvent. The best results were obtained with glacial acetic acid, without formation of tar, the yield being almost quantitative at temperatures up to 50°. Raising the temperature of nitration or increasing the concentration of the nitric acid slightly increases the proportion of *o*-nitrophenol formed. The best yields of the mononitrophenols were obtained with 10% nitric acid at 25°. The mixture of mononitrophenols was analysed by a method involving steam distillation of the *o*-nitrophenol and thermal analysis of the benzyl ethers of *m*- and *p*-nitrophenol.

The following derivatives of *m*-nitrophenol have been obtained: *acetate*, m. p. 55—56°; *picrate*, m. p. 170—171°; *benzyl ether*, m. p. 55°; *acetonyl ether*, m. p. 83—84°; acetophenonyl ether, m. p. 127°. R. B.

Action of Bromine on Methyl Esters of Phenolsulphonic Acids. Determination of Sulphur in Phenolsulphonic Esters and Salts. L. J. Simon and M. Frêrejacque (*Compt. rend.*, 1924, **178**, 1282—1284).—The action at a low temperature of bromine (1 atom) on methyl *o*-cresolsulphonate in methyl-alcoholic solution, yields (1) the *methyl bromo-o-cresolsulphonate*, m. p. 143°, which retains the methylating properties of the original compound and gives, in particular, the characteristic derivative of hexamethylenetetramine (cf. this vol., i, 665), and (2) the corresponding bromo-*o*-cresolsulphonic acid. At 100° a second bromine atom enters the nucleus, from which it displaces the sulphonic group, so that, if excess of bromine is employed, the sole products of the reaction are dibromo-*o*-cresol and sulphuric acid. Similar products are obtained from methyl anisole-*p*-sulphonate, which also takes up a second bromine atom only by elimination of the sulphonic group.

Methyl sulphate, which sulphonates the phenols so readily, has no action on their bromo derivatives, even at higher temperatures (cf. A., 1923, i, 462, 1098). This inertness is in harmony with the total elimination of the sulphonic group by bromine, which allows of the use of the latter for the determination of the sulphur in sulphonic derivatives of phenols. Desvergnes' method (A., 1920, ii, 563) gives satisfactory results with the methyl esters of various phenolsulphonic acids, and with the water-soluble additive products of the sulphonic esters with tertiary bases. No sulphuric acid is, however, liberated from the acyclic methanesulphonic and sulphoacetic acids. [Cf. *B.*, 1924, 444.] T. H. P.

Ultra-violet Absorption Spectra of Eugenol. G. THOMPSON (*J. Chem. Soc.*, 1924, **125**, 962; cf. *ibid.*, 1923, **123**, 1594).—The absorption spectrum of eugenol in thin films agrees closely with its spectrum in alcoholic solution, and the absorption bands previously recorded are therefore characteristic of the substance itself. Extinction coefficients could not be calculated, as it was not possible to measure the thickness of the films. R. B.

Catalytic Action. V. Catalytic Reduction of α- and β-Naphthyl Methyl Ethers. S. KOMATSU and S. KUMAMOTO (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 135—142).—The catalytic reduction of α-naphthol has previously been found to yield products containing *ar*- and *ac*-compounds in the ratio 1 : 9 (A., 1923, i, 782), whereas the presence of the amino group in α-naphthylamine favours the formation of *ar*-derivatives, the ratio of *ar*- to *ac*-compounds being 9 : 1. When α-naphthyl methyl ether is reduced by means of hydrogen and reduced nickel at 200°, the molecular ratio of *ar*- to *ac*-compounds is 19 : 81. β-Naphthyl methyl ether forms *ac*-derivatives less readily than does the α-ether, the molecular ratio of *ar*- to *ac*-products being 37 : 63. When reduced with sodium and boiling amyl alcohol, α- and β-naphthyl methyl ethers yield only *ar*-tetrahydronaphthyl ethers, but when β-naphthyl methyl ether is reduced with sodium and ethyl alcohol, β-*ar*-dihydronaphthyl methyl ether is obtained. C. J. S.

Preparation of 2- and 4-Nitro-α-naphthols. H. H. HODGSON and E. KILNER (*J. Chem. Soc.*, 1924, **125**, 807—811).—The 2- and 4-nitro compounds obtained by the nitration of aceto-α-naphthalide (cf. A., 1886, 754; T., 1905, **87**, 928) can be easily separated by hydrolysing the mixture with boiling 5% sodium hydroxide, and distilling the acidified solution with steam, whereby 2-nitro-α-naphthol is removed. The mixture was thus found to contain the 2- and 4-nitroaceto-α-naphthalides in the proportion 1 : 3. The poor yields of 2-nitro-α-naphthol obtained in the oxidation of 2-nitroso-1-naphthol with dilute nitric acid (A., 1892, 861) are due to the action of nitrous acid, liberated during the reaction, on the nitronaphthol. 4-Nitro-α-naphthol is attacked more rapidly than the 2-nitro compound. The addition of carbamide to the oxidation mixture raises the yield of 2-nitro-α-naphthol to 50% of the theoretical. Better results were obtained by using 100 vol. hydrogen peroxide, the yield being 50—60%. The by-products are soluble derivatives of phthalic acid. Ammonium 2-nitro-α-naphthoxide, in contrast with the nitronaphthol itself, can be distilled in steam without resinification. R. B.

Manufacture of G-Acid [β-Naphthol-6 : 8-disulphonic Acid], using Fuming Sulphuric Acid. T. KAWAGUCHI (*J. Chem. Ind. Japan*, 1923, **26**, 1233—1256).—When 1 part of β-naphthol is sulphonated with 5 parts of fuming sulphuric acid containing

20% of sulphur trioxide at 20—25° during 8 hours, G acid is the principal product, with β-naphthol-3 : 6-disulphonic acid (R acid) and -6-sulphonic acid (Schäffer acid) as by-products. Separating the last by partial crystallisation as barium salt, and G and R acids through the difference in solubility of their sodium salts in aqueous alcoholic solution, 2 grams of barium salt of Schäffer acid, 61 grams of sodium salt of G acid, and 22 grams of sodium salt of R acid were isolated from 50 grams of β-naphthol. Neglecting Schäffer acid, if G and R acids are separated as acid potassium and sodium salts, the yields of the two salts are 75 grams and 17 grams, respectively, from the same amount of β-naphthol.

K. K.

So-called Auxochromes and their Method of Action. A. Hantzsch (*Annalen*, 1924, **436**, 321—323).—A defence of the author's theory of isomeric change, in reply to Kaufmann (A., 1924, i, 37).

R. B.

Reaction of Resorcinol and of Phloroglucinol with Formaldehyde. A. Zamparo (*Boll. Chim. Farm.*, 1924, **63**, 161—164).—Resorcinol and phloroglucinol are the only ordinary phenolic compounds which react immediately in the cold to give coloured precipitates when 0·1 g. is dissolved in 3 c.c. of 95% alcohol and the solution is treated successively with 2 c.c. of 40% formaldehyde solution and 3 c.c. of concentrated hydrochloric acid; the two naphthols and thymol give precipitates soluble in alcohol. [Cf. *B.*, 1924, 445.]

T. H. P.

Dyes of the Aurin Type. II. H. Baines and J. E. Driver (*J. Chem. Soc.*, 1924, **125**, 907—910; cf. *ibid.*, 1923, **123**, 1214).—By the action of chloroform vapour on dry potassium phenoxide at 110° in the absence of oxygen, triphenyl orthoformate, m. p. 75°, and leucaurin, $CH(C_6H_4OH)_3$, are produced. The reaction proceeds more slowly with boiling chloroform, but the yield is greatly diminished by the presence of water and is not appreciably increased by using alcohol as solvent.

R. B.

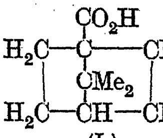
Catalytic Preparation of Benzyl Ethers. J. B. Senderens (*Compt. rend.*, 1924, **178**, 1412—1415).—The method previously described (this vol., i, 40) has now been applied to the preparation of benzyl ether, and of the mixed benzyl ethyl, benzyl propyl, benzyl *iso*propyl, benzyl butyl, benzyl *iso*butyl, and benzyl *iso*amyl ethers. For these mixed ethers, the boiling point rises, but the density diminishes as the molecular weight increases.

T. H. P.

Chemical Nature of the Naphthenic Acids. O. Aschan (*Ber.*, 1924, **57**, [*B*], 636—637).—A reply to a paper by Zelinsky and Pokrowskaja (this vol., i, 387) criticising work done by the author in 1892 (A., 1893, i, 209). The heptanaphthenecarboxylic acid was obtained pure by redistilling the methyl ester 30 times and boiled within 2°; it was probably purer than that obtained by Zelinsky and Pokrowskaja. The author had suggested in 1892

fore not novel. F. A. M.

Ketopinic Acid. Conversion into Norcamphane-1-carboxylic Acid. E. Wedekind [with C. Weinand] (*Ber.*, 1924, 57, [*B*], 664—666).—Ketopinic acid (cf. Wedekind, Schenk, and Stüsser, A., 1923, i, 346) is converted into its *semicarbazone*, m. p. 226°, which is transformed by sodium ethoxide and ethyl alcohol at 170—180° into *norcamphane*-1-*carboxylic acid* (I), m. p. 221—222°; the *copper, lead, mercury, silver,* and *zinc* salts are described. The *calcium* salt is particularly characteristic.


(I.)

The *phenylhydrazide*, m. p. 140°, and the *amide*, m. p. 192·5°, of ketopinic acid are described. The acid is associated to a considerable degree in benzene even in dilute solution. H. W.

Catalytic Action. VI. Catalytic Action of Reduced Copper on Acid Amides. S. Komatsu and M. Kurata (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 157—159).—The suggestion that at a high temperature reduced copper causes simultaneous dehydration and hydration has been confirmed by passing menthon*iso*oxime over the catalyst at 200°, whereby menthonitrile and decenoic acid were obtained. Benzamide when passed over reduced copper at 250° gives benzonitrile and benzoic acid, whilst acetamide (at 200°) yields acetonitrile and acetic acid. C. J. S.

Condensation of Nitriles with Thioamides. II. Acetonitrile with Thiobenzamide, and Benzonitrile with Thioacetamide. S. Ishikawa (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 93—98; cf. A., 1921, i, 728).—The combination of acetonitrile and thiobenzamide, induced by saturating their ethereal solution with dry hydrogen chloride, yields, not acetimino*iso*benzamide, but benzimino*iso*thiobenzamide. The fact that thioacetamide is found in the resulting solution indicates that the acetonitrile and thiobenzamide first condense similarly to benzonitrile and thiobenzamide, and that the condensation product is unstable and decomposes into benzonitrile and thioacetamide: $CH_3{\cdot}CN + NH{:}CPh{\cdot}SH \longrightarrow NH{:}CMe{\cdot}N{:}CPh{\cdot}SH \longrightarrow NH{:}CMe{\cdot}SH + C_6H_5{\cdot}CN$; equilibrium is reached when about 20% of the reacting compounds is converted into the final products. From benzonitrile and thioacetamide, benzimino*iso*thiobenzamide and thiobenzamide were obtained, the latter product representing about 71% of the benzonitrile.
T. H. P.

Electrolytic Oxidation of *p*-Nitrotoluene and *p*-Chlorotoluene to their respective Acids. R. Dunbrook and A. Lowy (*Trans. Amer. Electrochem. Soc.*, 1924, 45, 97—117).—Using 20% nitric acid as the electrolyte and platinum electrodes, *p*-nitrotoluene and *p*-chlorotoluene were oxidised to *p*-nitrobenzoic and *p*-chlorobenzoic acids, respectively. In the first case, the best conditions were with a current density of 4 amp. per sq. dm., at 100°, a current efficiency of 34·1% being obtained. In the second case, the current density was 0·5 amp. per sq. dm. and the current efficiency was 65%, but with acetic acid as solvent it rose to 96%. [Cf. *B.*, 1924, 444.] W. A. S.

[*p*-Aminobenzoic] Esters of Substituted Aminopropyl Alcohol. W. Schulemann, L. Schütz, and K. Meisenburg (U. S. Pat. 1474567).—dl-γ-*Dimethylamino*-αβ-*dimethylpropyl* p-*aminobenzoate* (crystalline *hydrochloride*) has m. p. 81—82°. dl-γ-*Diethylamino*-αβ-*diethylpropyl* p-*aminobenzoate hydrochloride* has m. p. 146°. γ-*Diethylamino*-β-*methyl*-α-*ethylpropyl* p-*aminobenzoate hydrochloride* has m. p. 178°. Chemical Abstracts.

Synthetic Anæsthetics [Alkylaminoalkyl *p*-Aminobenzoates. E. H. Volwiler and R. Adams (U.S. Pat. 1476934).—γ-*Butylallylaminopropyl* p-*aminobenzoate hydrochloride* forms white needles, m. p. 147°. *Butylallylamine*, from butyl bromide and allylamine, has b. p. 132—133°/760 mm. β-*Butylallylaminoethyl* p-*aminobenzoate hydrochloride* has m. p. 184°. The *hydrochlorides* of *propylallylaminopropyl* and iso*propylallylaminopropyl* p-*aminobenzoates* are viscous oils. iso*Amylallylaminoethyl alcohol*, b. p. 132—133°/55 mm. (obtained by heating ethylene oxide with *iso*amylallylamine at 60°) yields a p-*aminobenzoate hydrochloride*, m. p. 194—195°. Chemical Abstracts.

Identity of Abietic Acids Extracted from Different Colophonies. G. Dupont and R. Uzac (*Bull. Soc. chim.*, 1924, [iv], 35, 394—404; cf. Schulz, *Mon. Sci.*, 1920, **10**, 109).—Crude abietic acid, obtained by extracting colophony with 95% alcohol and hydrochloric acid, was purified by crystallisation to a constant rotatory power. In this way, pure abietic acid of m. p. 173°, and [α] −105° for the yellow light of the mercury arc, was obtained from colophony from the following sources: (1) *Pinus maritima*; (2) Aleppo pine; (3) *P. Laricio austriaca*; (4) *P. longifolia*; (5) *P. pinea*. Pimaric acid (A., 1921, i, 510), α- and β-alepic acids, and the sapinic acids are easily isomerised to abietic acid (β-pimarabietic acid) by the influence of hydrochloric acid. For these reasons, the authors do not regard abietic acid as a constituent of the natural gums, but as the final stable isomeric form of the constituents of these gums. The suggestion of Knecht and Hibbert (cf. A., 1919, i, 338) that abietic anhydride forms a constituent of colophony is rejected because abietic acid has been obtained from colophony in dry tubes at 130°, when no water was present to convert the anhydride into acid, and because abietic acid can be obtained from molten colophony in the presence of hydrogen chloride by merely seeding with a small quantity of the acid. It is suggested that the isomerisation of *l*-pimaric, α-sapinic, and β-sapinic acids takes place in two stages under the action of heat or hydrochloric acid, α-pimarabietic acid and α- and β-sapinabietic acids being formed intermediately. *d*-Pimaric acid is not isomerised under these conditions. R. B.

ααβ-Triphenylpropionic Acid and some of its Derivatives. (MLLE.) P. RAMART (*Bull. Soc. chim.*, 1924, [iv], **35**, 196—200).—A more detailed account of work already published (this vol., i, 171). S. K. T.

Calcium o-Benzyloxybenzoate. E. A. WILDMAN (U.S. Pat. 1481779).—Saponification of the product obtained by the interaction of methyl salicyate, benzyl chloride, and sodium ethoxide yields *o*-benzyloxybenzoic acid, m. p. 75°. The *calcium* salt, $Ca(O\cdot CO\cdot C_6H_4\cdot O\cdot CH_2Ph)_2$, is obtained by boiling the acid with water and calcium carbonate.

A New Iodosalicylic Acid. P. BRENANS and C. PROST (*Compt. rend.*, 1924, **178**, 1010—1012; cf. A., 1923, i, 797).—*4-Iodosalicylic acid*, colourless needles, turning brown at 200°, m. p. 228° (decomp.), was prepared from 4-nitro-*o*-toluidine by acetylation, oxidation to 4-nitroacetylanthranilic acid, deacetylation, and diazotisation to 4-nitrosalicylic acid, the ethyl ester of which was reduced; from the diazonium sulphate of the resulting amino compound hydriodic acid yielded *ethyl 4-iodosalicylate* (needles, m. p. 21°), which was hydrolysed. The *acetyl* derivative of the acid forms colourless crystals, m. p. 156°. H. J. E.

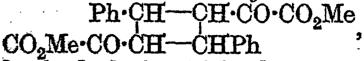
Iodinated m-Hydroxybenzoic Acids. P. BRENANS and C. PROST (*Compt. rend.*, 1924, **178**, 1285—1287).—Certain of the results obtained by the authors have been already published by Beyer (A., 1922, i, 37). The iodo-*m*-hydroxybenzoic acid, m. p. 226° (decomp.), prepared by Weselsky's method (A., 1875, 139) is identical with that obtained from 4-amino-*m*-hydroxybenzoic acid by way of the diazo compound, and is, therefore, 4-iodo-*m*-hydroxybenzoic acid. *4-Iodo-m-acetoxybenzoic acid* forms white crystals, m. p. 203°.

The iodohydroxybenzoic acid prepared from the amino-*m*-hydroxybenzoic acid obtained when 6-benzeneazo-*m*-hydroxybenzoic acid is reduced by means of stannous chloride and hydrochloric acid, is identical with that prepared from Griess' nitro-*m*-hydroxybenzoic acid (A., 1887, 485), which is hence the 6-nitro-acid. [Cf. Beyer, *loc. cit.*] T. H. P.

A New Iodo-p-hydroxybenzoic Acid. P. BRENANS and C. PROST (*Compt. rend.*, 1924, **178**, 1555—1557; cf. A., 1923, i, 1203).—The preparation of the second isomeride of iodo-*p*-hydroxybenzoic acid (2 : 4 : 1) is described. Treatment of the diazonium sulphate derived from 4-nitroanthranilic acid with potassium iodide yields 2-iodo-4-nitrobenzoic acid (cf. Willgerodt and Gartner, A., 1908, i, 877), which on reduction yields *2-iodo-4-aminobenzoic acid*, colourless needles, m. p. 188° (decomp.); *hydrochloride*, decomp. 210°; *sulphate*, white needles. The diazonium sulphate derived from this acid decomposes in aqueous solution, forming *2-iodo-4-hydroxybenzoic acid*, white, refractive needles, m. p. 215° (decomp.); *acetyl* derivative, m. p. 146°. J. W. B.

Phthalaldehydic Acid. L. SEEKLES (*Rec. trav. chim.*, 1924, **43**, 329—340).—Further details of the preparation of phthalaldehydic acid by the ozonisation of naphthalene are given (cf. A., 1923, i, 931). The normal phenylhydrazone of phthalaldehydic acid has not previously been described, as it readily loses water to form phenylphthalazone. It has now been obtained by the action of phenylhydrazine on the sodium salt of the acid. *Benzaldehydephenylhydrazone*-o-*carboxylic acid* forms a yellow precipitate, m. p. 100° (decomp.); the dark yellow *sodium* salt contains $4H_2O$, and the yellow *silver* salt turns brown in the light. Similar compounds were obtained using *p*-bromo- and *p*-nitro-phenylhydrazine. p-*Bromophenylphthalazone* forms fine, colourless needles, m. p. 169·5°; p-*nitrophenylphthalazone*, orange crystals, m. p. 259° (sintering from 228°). Hydrogen cyanide combines with the aldehydic group of phthalaldehydic acid in the normal manner, forming *o*-carboxymandelonitrile, from which *o*-carboxymandelic acid is obtained, by hydrolysis with hydrochloric acid, in the form of its lactone, phthalide-α-carboxylic acid. With acetic anhydride, phthalaldehydic acid forms a monoacetyl derivative, which must also have the phthalide structure, $C_6H_4{<}\begin{smallmatrix}CH(OAc)\\CO\end{smallmatrix}{>}O$. Its m. p. is 71°, not 60—63° as recorded elsewhere.

Comparison of the molecular refraction of phthalaldehydic acid in alcoholic solution with that of phthalide and phthalidecarboxylic acid shows that in this solvent phthalaldehydic acid has the phthalide structure, whilst in aqueous solution the aldehydic tautomeride is the more stable form. E. H. R.

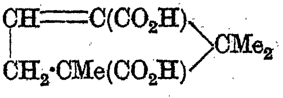
Benzylidenepyruvic Acid [Styrylglyoxylic Acid] and its Esters. I. The Action of Sunlight on Crystalline Methyl Styrylglyoxylate. M. REIMER (*J. Amer. Chem. Soc.*, 1924, **46**, 783—790).—Erlenmeyer's procedure for preparing styrylglyoxylic acid by condensing pyruvic acid and benzaldehyde in presence of sodium hydroxide (A., 1903, i, 698) has been improved and the yield increased to 80% of the theoretical. The *ethyl* ester is a yellow oil, b. p. 169—171°/7 mm.; the *methyl* ester forms long, yellow needles, m. p. 73—74°. After 1 month's exposure to sunlight, the methyl ester changes into a dimeric form, $(C_{11}H_{10}O_3)_2$, shown to be *methyl* 2 : 4-*diphenyl*cyclo*butane*-1 : 3-*diglyoxylate*,  $\begin{array}{l}Ph\cdot\underset{|}{C}H{-}\underset{|}{C}H\cdot CO\cdot CO_2Me\\ CO_2Me\cdot CO\cdot CH{-}CHPh\end{array}$, colourless crystals, m. p. 154°, which by hydrolysis yields the corresponding *acid*, m. p. about 187° (in some cases after melting at 110—116°, with evolution of gas, and again solidifying). When re-methylated with methyl alcohol, the acid gives an *ester*, $(C_{11}H_{10}O_3)_2$, m. p. 155°, not identical with the ester having m. p. 154°, but readily obtained from it by the action of hydrogen chloride in methyl alcohol. Oxidation of the above acid gives α-truxillic acid, which proves its constitution.

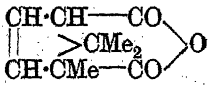
When methyl styrylglyoxylate dissolved in benzene is exposed to sunlight, a third isomeric *methyl* ester is obtained as colourless crystals, m. p. 117°. Hydrolysis of this ester gives an acid, m. p.

180°, which when esterified with methyl alcohol again forms the ester from which it had been produced. The free acid, when oxidised, is converted into δ-truxinic acid and is therefore concluded to be 3 : 4-*diphenyl*cyclo*butane*-1 : 2-*diglyoxylic acid.* C. J. S.

Saponins and Related Compounds. X. Urson. A. W. VAN DER HAAR (*Rec. trav. chim.*, 1924, **43**, 367—379).—The m. p. of chemically pure urson is 279—280° (cf. Dodge, A., 1919, i, 91). The generally accepted composition of urson, $C_{30}H_{48}O_3$, is incorrect, the correct formula being $C_{31}H_{50}O_3$. This formula explains the decomposition of urson, when distilled with zinc dust in a current of hydrogen, into sesquiterpenes, carbon dioxide, and water: $C_{31}H_{50}O_3 \longrightarrow 2C_{15}H_{24}+CO_2+H_2O$. The sesquiterpenes when heated with sulphur (Ruzicka's method) give an oil of which a *picrate*, m. p. 115—116°, was obtained; this is probably a picrate of a hydrocarbon of the naphthalene series, but is not identical with cadalene picrate. Urson contains one hydroxyl and one carboxyl group. *Acetylurson*, m. p. 200—201°, obtained by the action of acetic anhydride on urson, is deacetylated by boiling alcohol, consequently the "acetylurson" obtained by Gintl (A., 1893, i, 601) was urson itself. Dodge (*loc. cit.*) described a diacetylurson, and supposed urson to be a hydroxy-lactone, but his product probably contained occluded acetic anhydride. Methylation of urson takes place in the carboxyl group, giving methyl urson, which forms a *hydrate* containing $1H_2O$, m. p. 120°; anhydrous methyl urson has m. p. 165°, not 148° (cf. Nooyen, *Diss.*, Leyden, 1920). *Methyl acetylurson*, long, glistening needles, m. p. 245°, is more stable than acetylurson. The influence of the free carboxyl group on a neighbouring hydroxyl group has been also observed in the case of saponins (*e.g.*, hederagenin, A., 1922, i, 160). E. H. R.

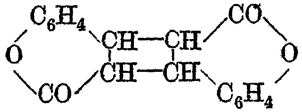
Steric Hindrance in Bridged Rings (Bredt's Rule) and the *meso-trans*-Position in Condensed *cyclo*Hexane Ring Systems. J. BREDT, H. THOUET, and J. SCHMITZ (*Annalen*, 1924, **437**, 1—13).—The author adduces facts in agreement with his rule (cf. A., 1902, i, 374; 1913, i, 281; 1917, i, 655) that double bonds cannot exist in conjunction with the "bridge-heads" in bridged *cyclo*hexane structures. He now shows that a bridged (7-membered) ring of this kind cannot be formed. Thus, such a dicarboxylic acid as dehydrocamphoric acid (I) does not yield a simple anhydride, but gives ultimately the anhydride of *iso*dehydrocamphoric acid (II):

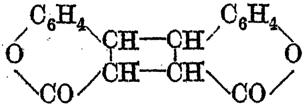
(I.)

$$\left.\begin{array}{l} CH{=\!=}C(CO_2H) \\ | \\ CH_2\cdot CMe(CO_2H) \end{array}\right> CMe_2$$


$$\left.\begin{array}{l} CH\cdot CH{-\!-}CO \\ \|\quad >CMe_2 \\ CH\cdot CMe{-\!-}CO \end{array}\right> O$$
(II.)

Silver dehydrocamphorate and dehydrocamphoryl chloride heated together produce an amorphous *dianhydride*, sintering at 120°, but having no definite m. p. Dehydrocamphoric acid heated with acetyl chloride yields the acid chloride and a *mixed anhydride*, and the latter compound is also formed when the acid is heated with acetic anhydride. It forms a syrupy mass; when heated further, it decomposes, giving a *poly-anhydride* of dehydrocamphoric acid, a vitreous substance, which when distilled in a vacuum yields *iso-dehydrocamphoric anhydride*, stout crystals, m. p. 184°. The conclusion that dehydrocamphoric acid can yield no simple anhydride is supported by steric considerations, and for these reasons the author concludes that the anhydrides obtained by Perkin (T., 1894, **65**, 572, 890) are likewise polymeric compounds. W. A. S.

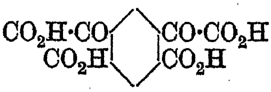
Biscoumaric Acids. A. W. K. de Jong (*Rec. trav. chim.*, 1924, **43**, 316—322).—The author suggests that the biscoumarins have structures similar to those of the truxillic and truxinic acids (A., 1923, i, 574). There are thus four possible isomerides, two corresponding with the plane formula (I) and two with (II):


(I.)


(II.)

The biscoumaric acid of Ström (A., 1904, i, 505) is formed by a method analogous to the formation of α-truxillic acid from α-cinnamic acid. It should therefore be called α-biscoumaric acid, and the biscoumarin derived from it is α-biscoumarin, m. p. 318° (decomp.). This should have formula I. It forms a *dimethyl ether*, colourless needles, m. p. 133°, which when hydrolysed gives α-biscoumaric acid dimethyl ether, m. p. 261—262°, which appears to be identical with the product obtained by Bertram and Kürsten by the action of light on coumaric acid methyl ether. When the dimethyl ether is heated with acetic anhydride, it forms *γ-biscoumaric acid dimethyl ether anhydride*, m. p. 186—187°, which when hydrolysed gives *γ-biscoumaric acid dimethyl ether*, brilliant needles, m. p. 234°. Another acid, *ε-biscoumaric acid*, m. p. 262°, was obtained by the action of fused potassium hydroxide on α-biscoumaric acid. The biscoumarin obtained by Ciamician and Silber (A., 1914, ii, 234) and called by them dihydrocoumarin, by the action of light on coumarin, is now called ζ-biscoumarin; m. p. 262°. This corresponds with formula II, and it is proposed to call the corresponding acids *biscoumarinic acids*, to correspond with the truxinic acids. *ζ-Biscoumarinic acid* is a dibasic acid, m. p. 245°, forming fine needles which soon grow into larger crystals. *Dimethyl ζ-biscoumarinate dimethyl ether* forms yellow crystals, m. p. 112—113°; *ζ-biscoumarinic acid dimethyl ether*, m. p. 134°. By heating with fused potassium hydroxide ζ-biscoumarinic acid is converted into *δ-biscoumarinic acid*, m. p. 157°. The hydrodicoumarin obtained by Dyson (*Chem. Soc. Trans.*, 1887, **51**, 66), by reducing dicoumarin with sodium amalgam, is not identical with ζ-biscoumarin, as supposed by Ciamician and Silber. By hydrolysis, it gives a monobasic acid. E. H. R.

Preparation of Pyromellitic Acid. J. von Braun and G. Lemke (*Ber.*, 1924, **57**, [*B*], 681—682).—The oxidation of octahydroanthracene with alkaline permanganate yields an acidic product of approximately the formula $C_{12}H_6O_{10}$, which is probably a mixture of the two isomeric diphthalonic acids :



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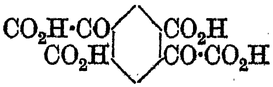


These could not, however, be separated. Further oxidation with acid permanganate gave a nearly quantitative yield of pyromellitic acid. From 30 g. of octahydroanthracene 41 g. of practically pure pyromellitic acid were obtained. F. A. M.

Action of Aluminium Alkoxides on Mixtures of Aldehydes. N. A. Orloff (*Bull. Soc. chim.*, 1924, [iv], **35**, 360—363; cf. A., 1907, i, 282).—The action of aluminium ethoxide on three mixtures of aldehydes has been studied. Benzaldehyde and *iso*butyraldehyde gave a product from which three fractions were obtained, the first consisting of *iso*butyl *iso*butyrate, the second of *iso*butyl benzoate (19·3%) and benzyl *iso*butyrate (80·7%), and the third of pure benzyl benzoate. From a mixture of *iso*butyraldehyde and acetaldehyde, in addition to *iso*butyl *iso*butyrate, ethyl acetate, and aldolic products, a mixture, b. p. 110—117·5°, was obtained consisting of *iso*butyl acetate (75%) and ethyl *iso*butyrate (25%). Benzaldehyde and acetaldehyde gave, besides ethyl acetate, benzyl benzoate, and unchanged benzaldehyde, a mixture of benzyl acetate (96·2%) and ethyl benzoate (3·8%). The author concludes that of the two possible mixed esters, that one will be formed in larger amount in which the aldehyde of higher molecular weight yields the alcoholic component. R. B.

Catalytic Hydration of Schiff's Bases. A. Maihle (*Bull. Soc. chim.*, 1924, [iv], **35**, 379—382; cf. A., 1919, i, 395; 1920, i, 380).—Schiff's bases are easily hydrolysed when vaporised in a current of steam and passed over catalysts such as thoria and alumina heated at 400°. In this way, benzylideneaniline, for example, yields benzaldehyde and aniline. In the presence of vapours of methyl or ethyl alcohol the amine is immediately alkylated, the product of the reaction being the corresponding dialkylamine, but in the presence of higher alcohols such as propyl alcohol, alkylation does not take place. R. B.

Thermochemical Researches on Stereoisomeric Aldoximes. W. Swientoslawski and M. Popoff (*Bull. Soc. chim.*, 1924, [iv], **35**, 137—144).—Measurement of the heat evolved when sodium hydroxide or hydrochloric acid reacts with a stereoisomeric aldoxime (benzaldoxime, *m*-nitrobenzaldoxime) shows that the :N·OH group is more strongly acidic in the α-(*anti*)-aldoximes than in the β-(*syn*-)-aldoximes. The heat of solution in water is always negative, the β-isomeride having the higher absolute value.

Dry hydrogen chloride converts concentrated ethereal solutions of α-aldoxime into the β-stereoisomeride, but not always quantitatively. When a mixture of the two forms results, the α-aldoxime is in greater proportion the greater the speed of the conversion. A thermochemical method for the quantitative analysis of these mixtures is developed. Mixtures containing up to 40% of the hydrochloride of α-benzaldoxime and of α-*m*-nitrobenzaldoxime were prepared.

The heat of conversion in ether solution of α- into β-benzaldoxime is —0·98 Cal.; that for α- into β-*m*-nitrobenzaldoxime is —1·18 Cal. The heats of transformation in the free state are +2·64 Cal. ($\alpha_{\text{liq.}}$ to β_{solid}) and —1·25 Cal. (α_{solid} to β_{solid}), respectively. E. E. T.

Derivatives of *p*-Nitrobenzaldehyde. II. C. G. King and A. Lowy (*J. Amer. Chem. Soc.*, 1924, **46**, 757—762; cf. A., 1921, i, 337).—The following new *p*-nitrobenzylidene compounds have been prepared: p-*nitrobenzylidene*-o-*bromoaniline*, m. p. 106°; -m-*bromoaniline*, m. p. 102°; -2 : 6-*dibromoaniline*, m. p. 137°; -2 : 4 : 6-*tribromoaniline*, m. p. 142·5°; -3-*bromo*-4-*toluidine*, m. p. 112°; -p-*xylidine*, m. p. 100°; -o-*nitroaniline*, m. p. 169°. All form yellow needles except the last, which forms small plates.

p-Nitrobenzaldehyde condenses with 2 mols. of phenol by Danckworth's method, giving *p*-nitro-*p′p″*-dihydroxytriphenylmethane, which forms a 3′ : 5′ : 3″ : 5″-*tetrabromo* derivative,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}(C_6H_2Br_2{\cdot}OH)_2,$$

small, yellow plates, m. p. 215°; *diacetyl* derivative, m. p. 168°.

The condensation product from resorcinol and *p*-nitrobenzaldehyde gave, on bromination, a *dibromo*-p-*nitrotetrahydroxytriphenylmethane*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}[C_6H_2(OH)_2Br]_2$, a yellow, amorphous powder which turns red at 170° and chars above 200°. From *o*-nitrophenol and the nitro-aldehyde was obtained 4 : 3′ : 3″-*trinitro*-4′ : 4″-*dihydroxytriphenylmethane*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}[C_6H_3(OH)NO_2]_2$, an orange, amorphous powder, m. p. 177°. The condensation product obtained from thymol and *p*-nitrobenzaldehyde was brominated and gave a *dibromo* derivative, $NO_2{\cdot}C_6H_4{\cdot}CH{:}[C_6HMePrBrOH]_2$, light orange crystals, m. p. 115°; *dibenzoyl* derivative, a pale yellow, amorphous powder, m. p. 82°. C. J. S.

Electrolytic Preparation of Salicylaldehyde from Salicylic Acid. K. S. Tesh and A. Lowy (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 325—333).—Sodium salicylate is reduced electrolytically in the usual type of diaphragm cell with a mercury cathode, sodium sulphate being used as anolyte and a mixture of boric acid and sodium sulphate as catholyte. A current density of 6 amp. per sq. dm. is employed, and the temperature maintained at 15—18°; less aldehyde and more resinous matter is obtained at higher temperatures. The salicylaldehyde produced is fixed as soon as formed by progressive addition of sodium hydrogen sulphite, and is recovered by acid hydrolysis and distillation with steam. The best yield obtained is 55% of the theoretical. W. T. K. B.

Thermochemical Researches on Ketoximes. Non-stereoisomeric Ketoximes. A. Dorabialska (*Bull. Soc. chim.*, 1924, [iv], **35**, 145—152).—A thermochemical investigation of dimethyl, [illegible] and phenyl methyl ketoximes (cf. Swientoslawski and Popoff, p. 645). According to theory two stereoisomeric phenyl methyl ketoximes should exist, but only one could be obtained, treatment of ether or toluene solutions of the oxime with hydrogen chloride failing to cause any conversion. The heats of formation of the hydrochlorides of the oximes in ether solution differ but little from those of the aldoximes; they diminish with increasing acidity. Phenyl methyl ketoxime is more acidic than its constitution indicates. This is probably due to the ketoxime having the α-structure, since α-aldoximes are more acidic than the β-forms. The heat of solution of the hydrochlorides in 10% sodium hydroxide decreases as the acidity of the ketoxime increases. The heat is made up of four portions, viz., heat of solution of the hydrochloride in water (which is negative and less than that of the aldoximes), heat of decomposition (negative) of the hydrochloride into hydrochloric acid and oxime, heat of reaction of the oxime with sodium hydroxide, and heat of neutralisation of hydrochloric acid and sodium hydroxide. The parallel increase of the first two of these quantities is the cause of the decrease of the total heat with increasing acidity. E. E. T.

Ethyl Mercaptol of Phenyl Ethyl Ketone; a New Disulphone. A. Schmidt (*Bul. Soc. Chim. România*, 1924, **6**, 34—36).—On passing a stream of hydrogen chloride into a mixture of phenyl ethyl ketone (1 part) and ethyl mercaptan (2 parts) together with a small amount of anhydrous zinc chloride, the *ethyl mercaptol* of *phenyl ethyl ketone*, $CEtPh(SEt)_2$, a colourless oil of disagreeable odour, is formed. On oxidation with potassium permanganate in presence of dilute sulphuric acid, the corresponding *disulphone* is obtained in small yield as colourless, monoclinic plates, m. p. 113·5°. A. E. C.

Two Oximes of α-Ketotetrahydronaphthalene. H. Inoue (*J. Chem. Ind. Japan*, 1923, **26**, 1335—1338; cf. *Chem. Soc. Trans.*, 1899, **75**, 150).—The oxime of α-ketotetrahydronaphthalene, obtained by catalytic reduction of α-naphthol, is separated by steam distillation into a more volatile isomeride, A, colourless needles, m. p. 88—89°, and a less volatile, B, large, colourless prisms, m. p. 102—103°. By the Beckmann rearrangement, A gives B and B gives a nitrile-like liquid and another isomeric compound, C, colourless needles or prisms, m. p. 134—136°. A and B are probably stereoisomeric forms of the ketoxime. K. K.

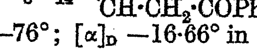
Influence of Constitution on the Rotatory Power of Optically Active Substances. XVI. Acetylene Derivatives, Ketones, Carbylamines. H. Rupe (*Annalen*, 1924, **436**, 184—204; cf. A., 1909, i, 927).—A comparison has been made between the rotatory powers of compounds containing acetylenic linkings and the corresponding ethylenic and saturated compounds. Phenylacetylenylborneol, its dihydro- and tetrahydro-derivatives all exhibit normal rotation dispersion, and the ethylenic compound shows the greatest specific rotatory power. 1 : 2 : 2 : 3-Tetramethyl*cyclo*pentyl phenylacetylenyl ketone exhibits a large anomalous rotation-dispersion, whilst its dihydro and tetrahydro derivatives and also an isomeric ethylenic compound obtained by the condensation of 1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl methyl ketone with benzaldehyde (Rupe and Kloppenburg, A., 1919, i, 539) are nearly normal. Amylcarbylamine, hexonitrile, hexylamine, and benzylidenehexylamine all exhibit anomalous rotation-dispersion, which is total in the case of the first substance. 3-Methyl*cyclo*hexylcarbylamine and 3-methyl*cyclo*hexylamine show very similar dispersions and it is doubtful whether these are normal or not. α-Camphorcarbimide exhibits an enormous specific rotation in comparison with the other members of the series.

Phenylacetylenylborneol, $C_8H_{14}<\begin{matrix}CH_2\\ C(OH)\cdot C{:}CPh\end{matrix}$, from magnesium phenylacetylenyl bromide and camphor, has b. p. 190°/13 mm. or 125—126°/0·1 mm., m. p. 44—45°, $[\alpha]_D^{20}$ −27·37° in 10% benzene solution.

Styrylborneol, $C_8H_{14}<\begin{matrix}CH_2\\ C(OH)\cdot CH{:}CHPh\end{matrix}$, was obtained from the preceding compound by regulated reduction with hydrogen and a nickel catalyst in a mixture of aqueous alcohol and ethyl acetate. It forms a colourless, viscous oil, b. p. 183—186°/11 mm., 106—107°/0·1 mm.; $[\alpha]_D$ −107·7° in 10% benzene solution.

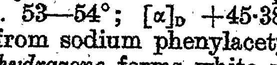
β-*Phenylethylborneol*, $C_8H_{14}<\begin{matrix}CH_2\\ C(OH)\cdot CH_2\cdot CH_2Ph\end{matrix}$, was obtained from the preceding compound by further reduction under identical conditions. It is a colourless, limpid oil, b. p. 176—179°/14 mm., 138—140°/0·5 mm.; $[\alpha]_D$ −25·45° in 10% benzene solution. By boiling for 12 hours with formic acid, it is dehydrated, and β-*phenylethylbornylene*, a limpid oil, b. p. 165—168°/12 mm., is formed.

Phenylacetylenylborneol, on boiling with formic acid, undergoes rearrangement to a *ketone* probably having the formula



$$C_8H_{14}<\begin{matrix}CH_2\\ C{:}CH\cdot COPh\end{matrix},$$

a yellowish-brown oil, b. p. 193—196°/12 mm., $[\alpha]_D$ −39·97° in 10% benzene solution; *semicarbazone*, white prisms, m. p. 155—156°; *phenylhydrazone*, yellow needles, m. p. 120—121°. By catalytic reduction, the ketone gives *phenyl camphanylmethyl ketone*,



$$C_8H_{14}<\begin{matrix}CH_2\\ CH\cdot CH_2\cdot COPh\end{matrix},$$

white plates, m. p. 75—76°; $[\alpha]_D$ −16·66° in 10% benzene solution; *phenylhydrazone*, yellow needles, m. p. 110—111°; *semicarbazone*, m. p. 179—181°. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentyl phenylacetylenyl ketone*, $C_8H_{14}Me\cdot CO\cdot C{:}CPh$, was synthesised from magnesium phenylacetylenyl bromide and campholic chloride, and formed needles, m. p. 53—54°; $[\alpha]_D$ +45·38° in 10% benzene. It was also obtained from sodium phenylacetylene and campholic chloride. The *phenylhydrazone* forms white needles, m. p. 137—138°; the *hydrazone*, needles, m. p. 123—124°. On warming with methyl-alcoholic potash, the ketone gave a viscous, yellow oil, b. p. 245—247°/13 mm., apparently an additive compound with [illegible] methyl alcohol. This methoxy compound gave a *phenyl-*

hydrazone, m. p. 144—145°. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentyl styryl ketone*, from the acetylenic compound by reduction as before, is a pale yellow, somewhat viscous oil, b. p. 192—194°/12 mm., $[\alpha]_D$ +45·31° in benzene.

Its isomeride (cf. *supra*) has $[\alpha]_D$ +54·24° in 10% benzene solution. 1 : 2 : 2 : 3-Tetramethyl*cyclo*pentyl β-phenylethyl ketone may be obtained by the reduction of the acetylenic ketone (b. p. 178—181°/12 mm.; $[\alpha]_D$ +40·51° in 10% benzene solution) or of Rupe and Klottenburg's ketone (b. p. 188—189°/13 mm.; $[\alpha]_D$ +48·24° in 10% benzene solution), as well as by the method of Rupe and Jäggi (A., 1922, i, 840); (b. p. 178—181°/10 mm. and $[\alpha]_D$ +38·84° in 10% benzene solution).

Active amylcarbylamine has b. p. 137—138°/745 mm.; $[\alpha]_D$ +0·35° in benzene solution. Hexonitrile, hexylamine, and benzylidenehexylamine have $[\alpha]_D$ +0·76°, 0·86°, 1·41°, respectively. *Methyl*cyclo*hexylamine*, from the oxime of 3-methyl*cyclo*hexanone, has $[\alpha]_D$ −2·09°. By the action of chloroform and potassium hydroxide, 3-*methyl*cyclo*hexylcarbylamine* was obtained as an oil, b. p. 67—69°/10 mm.; $[\alpha]_D$ −0·77°. *Benzylidenehexylamine* is a colourless liquid, b. p. 130—132°/13 mm. A. E. C.

Equilibrium between Benzaldehyde and Benzoin. A. Lachman (*J. Amer. Chem. Soc.*, 1924, **46**, 708—723).—The condensation of 2 mols. of benzaldehyde to give 1 mol. of benzoin requires the combined action of hydroxyl and cyano ions. These catalysts also reverse the condensation, but at the same time they convert benzoin into benzyl benzoate and benzoic acid, this step not being reversible. When benzoin is heated at 300°, it is partly converted into benzaldehyde; under the same conditions, benzaldehyde yields no benzoin, but forms benzyl benzoate, benzoic acid, toluene, and dibenzyl ether. The benzoin and Cannizzaro condensations can be accounted for by two assumptions. Benzaldehyde combines with M·OH(or ·OR) to form the compound CHPh(OM)(OH) (A), in which ·OH is the more labile group; and with hydrogen cyanide to form CHPh(CN)(OH) (B), in which H is more labile. A reacts with benzaldehyde by transfer of hydroxyl to yield benzyl benzoate; it reacts with B according to the equation CHPh(CN)(OH) + CHPh(OH)(OK) = CPh(CN)(OK)·CH(OH)Ph + H_2O; if both benzaldehyde and B are present, it reacts with both; if A is absent, as in acidified solutions, benzoin fails to form. The unique function of the cyano ion as the only catalyst which will convert benzaldehyde into benzoin also becomes clearer. Benzaldehyde forms additive products of the general type CHPh(OH)(X) with sodium hydrogen sulphite, hydrogen chloride, and hydrogen cyanide, but of these the last is the only one capable of existing under conditions necessary for the presence of A, *i.e.*, alkaline solution. A method is described for preparing benzoin without the use of alcohol. C. J. S.

Optically Active β-Phthalimino-β-phenylpropiophenones. A. McKenzie and T. M. A. Tudhope (*J. Chem. Soc.*, 1924, **125**, 923—930; cf. *ibid.*, 1921, **119**, 69).—In the preparation of *r*-β-amino-β-phenylpropionic acid from hydroxylamine and cinnamic acid (cf. A., 1905, i, 577), besides acetophenoneoxime, 3-phenyl*iso*-oxazolone, m. p. 149—151°, is produced (cf. A., 1906, i, 955; 1912, i, 453). *r*-β-Phthalimino-β-phenylpropionic acid was resolved into its optically active components with cinchonine in rectified spirit. From the more sparingly soluble cinchonine salt was separated d-β-*phthalimino*-β-*phenylpropionic acid*,

$$C_6H_4{:}C_2O_2{:}N{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H,$$

glassy rosettes, m. p. 150—151°, having $[\alpha]_D$ $-5{\cdot}5°$ in ethyl acetate, and $-2{\cdot}2°$ in ethyl alcohol. The same active acid was obtained by the resolution of *r*-β-amino-β-phenylpropionic acid (cf. A., 1910, i, 622) and heating the *d*-amino-acid with phthalic anhydride. In spite of its lævorotation in ethyl acetate, this acid is accordingly designated as *d*-β-phthalimino-β-phenylpropionic acid, taking *d*-β-amino-β-phenylpropionic acid as the reference compound. In methyl alcohol, the phthalimino acid is slightly dextrorotatory. Thionyl chloride converts the *d*-phthalimino acid into its acid chloride from which, by the Friedel-Crafts reaction, is obtained d-β-*phthalimino*-β-*phenylpropiophenone*,

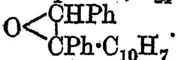
$$C_6H_4{:}C_2O_2{:}N{\cdot}CHPh{\cdot}CH_2{\cdot}COPh,$$

m. p. 116—117°, $[\alpha]_D^{15}$ $-127{\cdot}1°$ in benzene and $[\alpha]_D^{13}$ $-96{\cdot}2°$ in acetone. l-β-*Phthalimino*-β-*phenylpropiophenone* was similarly obtained from the *l*-phthalimino acid. Hydrolysis of the lævorotatory *d*-ketone with alcoholic sodium hydroxide yields d-β-*benzoyl*-α-*phenylethylphthalamic acid*, $COPh{\cdot}CH_2{\cdot}CHPh{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$, feathery crystals, m. p. 147—147·5°, $[\alpha]_D^{16{\cdot}5}$ $+38{\cdot}8°$ in ethyl alcohol, which on hydrolysis with a mixture of concentrated hydrochloric acid and glacial acetic acid yields phthalic acid and the lævorotatory *d*-β-phthalimino-β-phenylpropiophenone, dehydration as well as hydration of the phthalamic acid taking place. R. B.

Migration of Groups in Derivatives of Benzoin and Desylamine. A. McKenzie and R. Roger (*J. Chem. Soc.*, 1924, **125**, 844—854; cf. A., 1923, i, 213, 333, 788).—The dehydration of methylhydrobenzoin with concentrated sulphuric acid yields a methyldeoxybenzoin, m. p. 50—52° (cf. Tiffeneau and Orékhov, A., 1920, i, 672; 1921, i, 565; Lévy, A., 1921, i, 860), from which two semicarbazones were obtained, m. p. 213—215° (cf. A., 1920, i, 672) and 159—160°. The methyldeoxybenzoin thus appears to exist in two forms, one melting at 50—52° (cf. A., 1888, 703) and the other at 58—59°. Both forms are converted into ααβ-triphenyl-α-propanol, m. p. 88—89°, with magnesium phenyl bromide. A small amount of *as*-diphenylacetone is also formed in the dehydration of the glycol as a result of slight semipinacolin transformation. The dehydration of αα-diphenylpropane-αβ-diol with either dilute or concentrated sulphuric acid (cf. A., 1906, i, 724) yields *as*-diphenylacetone: $OH{\cdot}CPh_2{\cdot}CHMe{\cdot}OH \longrightarrow CHPh_2{\cdot}COMe$, vinyl dehydration being the only change which occurs. The ketone has m. p. 58·5—59·5° and its semicarbazone m. p. 169—170° (cf. A., 1906, i, 581). β-Hydroxy-αβ-diphenylpropylamine on treatment with sodium nitrite in acetic acid solution undergoes semipinacolinic deamination and yields *as*-diphenylacetone, m. p. 45—47° when freshly prepared, rising to 58—59° after 4 weeks. The transformation: $OH\cdot CPhMe\cdot CHPh\cdot NH_2 \longrightarrow COMe\cdot CHPh_2$, is in marked contrast to the vinyl dehydration of methylhydrobenzoin: $OH\cdot CPhMe\cdot CHPh(OH) \longrightarrow CHPhMe\cdot COPh$. Other examples of the action of nitrous acid on amino-alcohols cited by McKenzie and Richardson (T., 1923, **123**, 79) are interpreted on similar lines. In the light of this work, the product, $C_{21}H_{18}O$, m. p. 121·5—122°, obtained by McKenzie and Richardson by the action of nitrous acid on γ-hydroxy-αγγ-triphenyl*iso*propylamine,

$$CH_2Ph\cdot CH(NH_2)\cdot CPh_2\cdot OH,$$

is benzyldeoxybenzoin (cf. Meyer and Oelkers, A., 1888, 703), semipinacolinic deamination taking place. A further example of this change is the conversion by nitrous acid of β-hydroxy-αββ-triphenylethylamine into phenyldeoxybenzoin.

The dehydration of αβ-diphenyl-β(α-naphthyl)-ethane-αβ-diol, m. p. 204—205° (cf. A., 1904, i, 742), with dilute sulphuric acid yields a compound, $C_{24}H_{18}O$, m. p. 180—181°, probably the ethylenic oxide,  $O<\begin{matrix}CHPh\\ |\\ CPh\cdot C_{10}H_7\end{matrix}$. Concentrated sulphuric acid yields an isomeride, m. p. 108—109°, identical with the product obtained by the action of nitrous acid on β-hydroxy-αβ-diphenyl-β-naphthylethylamine (T., 1923, **123**, 79). R. B.

Stereochemical Investigations in the Phenyl Styryl Ketone Series. Certain Derivatives of Dibenzoylmethane and of Phenyl Styryl Ketone. C. DUFRAISSE and A. GILLET (*Compt. rend.*, 1924, **178**, 948—950).—The phenyl β-alkoxystyryl ketones, $COPh\cdot CH{:}CPh\cdot OR$ (A., 1923, i, 113) combine with bromine without forming any appreciable proportion of hydrogen bromide, but the dibromo compounds obtained, $COPh\cdot CHBr\cdot CBr(Ph)\cdot OR$, are extremely sensitive to the action of moisture and undergo immediate transformation into bromodibenzoylmethane, $COPh\cdot CHBr\cdot COPh$. When special precautions are taken, it is, however, possible to replace by a second alkoxy group the bromine atom of the $\cdot CBr(Ph)\cdot OR$ group. In this way, good yields of the following monoacetals of bromodibenzoylmethane were obtained: *phenyl α-bromo-ββ-dimethoxy-β-phenylethyl ketone*, $CHBrBz\cdot CPh(OMe)_2$, m. p. 91°; corresponding *diethoxy* compound, $CHBrBz\cdot CPh(OEt)_2$, m. p. 72°; *dipropoxy* compound, $CHBrBz\cdot CPh(OPr)_2$, m. p. 84°. Of the two possible racemic compounds represented by the formula, $CHBrBz\cdot CPh(OMe)\cdot OEt$, only one, m. p. 90°, has yet been obtained.

These acetals are white compounds and are particularly sensitive towards acids, which convert them immediately into bromodibenzoylmethane. When heated, they lose 1 mol. of an alcohol giving pale yellow phenyl α-bromo-β-alkoxystyryl ketones, of which the following have been prepared: *phenyl α-bromo-β-methoxystyryl ketone*, $CBrBz{:}CPh\cdot OMe$, m. p. 72° (stable form); corresponding β-*ethoxy* compound, $CBrBz{:}CPh\cdot OEt$, m. p. 76° (stable form); and β-*propoxy* compound, $CBrBz{:}CPh\cdot OPr$, m. p. 49°.

These undergo hydrolysis when heated with a dilute acid, bromodibenzoylmethane being formed. The action on them of an alkali alkoxide results in the fixation at the double linking of an alcohol molecule, the resulting monoacetals being either symmetrical or unsymmetrical.

The phenyl α-bromo-β-alkyloxystyryl ketones are prone to exist in several forms, each having characteristic crystallographic constants, melting point, and solubility. Thus, the methoxy compound exhibits two forms, m. p. 64° and 72°, and the ethoxy compound, three forms, m. p. 65°, 73°, and 76°. The form with the highest melting point is the most stable, and when it has once made its appearance in a laboratory, the preparation there of the other form or forms is impossible unless the precautions employed in obtaining pure cultures of bacteria are taken.

The unstable form of phenyl α-bromo-β-methoxystyryl ketone, m. p. 64°, is isomorphous with the stable form of phenyl αβ-dibromostyryl ketone, m. p. 80°, and with the unstable form, m. p. 71°, of one of the di-iodo derivatives of phenyl styryl ketone. T. H. P.

Stereoisomeric Semicarbazones. F. J. Wilson and R. M. Macaulay (*J. Chem. Soc.*, 1924, **125**, 841—844; cf. *ibid.*, 1912, **101**, 1482; 1913, **103**, 377, 1504).—By exposure to ultra-violet light dypnone semicarbazone, $CPhMe{:}CH{\cdot}CPh{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$, m. p. 151°, has been converted into a second of the four stereoisomerides required by theory. The new semicarbazone, m. p. 175—176°, is obtained in a yield of 33% of theory, and partial reconversion is effected on further exposure. Similarly, the δ-phenylsemicarbazone of mesityl oxide, m. p. 134°, yields about 33% of a more soluble *stereoisomeride*, m. p. 99—101°, reconversion being accomplished by heating in alcoholic solution. The semicarbazone of phenyl β-phenylstyryl ketone, m. p. 171—172° (cf. A., 1916, i, 821) yields, in the same way, the second stereoisomeric carbazone required by theory, a pale yellow, microcrystalline powder, m. p. 204—205°, partial transformation of either stereoisomeride taking place on exposure in alcoholic solution. Attempts to obtain a stereoisomeride of styryl *iso*butenyl ketone semicarbazone, $CMe_2{:}CH{\cdot}C({:}N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH{:}CHPh$, m. p. 168°, were unsuccessful. In the preparation of the semicarbazone, a small quantity of a substance, m. p. 221—222°, possibly the semicarbazide-semicarbazone,

$$CMe_2(NH{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH_2{\cdot}C({:}N{\cdot}NH{\cdot}CO{\cdot}NH_2){\cdot}CH{:}CHPh,$$

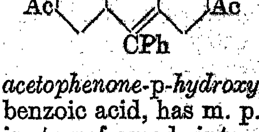
was obtained. Attempts to obtain stereoisomerides of the semicarbazones of benzylacetone, benzylacetophenone, and styryl methyl ketone were also unsuccessful. R. B.

Indones. V. Conversion of 3-Phenyl-2-methylindone into Diphenyldimethyltruxones by the Action of Ultra-violet Rays. [illegible] Fazi (*Gazzetta*, 1924, **54**, 85—88; cf. A., 1920, i, 316; 1921, [illegible]—It has been shown previously that, when treated with concentrated sulphuric acid, ethyl β-hydroxy-ββ-diphenyl-α-methylpropionate yields 3-phenyl-2-methylindone, whereas ethyl β-hydroxy-ββ-diphenylpropionate gives 3-phenylindone and the two diphenyltruxones (A., 1915, i, 1063; 1916, i, 151; 1920, i, 316; 1921, ii, 357). Under the same conditions, 3-phenyl-2-methylindone yields no truxone, but may be recovered unchanged from the emerald-green solution formed.

The two *diphenyldimethyltruxones* (cf. A., 1920, i, 317) are, however, formed when a benzene solution of 3-phenyl-2-methylindone is subjected in a quartz tube to the influence of the ultraviolet light from a quartz mercury vapour lamp. The first *isomeride* forms pale, canary-yellow crystals, m. p. 259—260°; the second *isomeride* forms white crystals, m. p. 307—308°, appears to be phototropic, and, after repeated crystallisation from alcohol, yields 3-phenyl-2-methylindone when treated with concentrated sulphuric acid. T. H. P.

The Benzil Rearrangement. VI. A. LACHMAN (*J. Amer. Chem. Soc.*, 1924, **46**, 779—782; cf. A., 1923, i, 784, 785).—In the benzil rearrangement there are two opposing reactions: one, consisting of intramolecular oxidation and reduction, giving benzilic acid; and the other, a process of rupture, producing benzaldehyde and ethyl benzoate. The first reaction will not occur in the absence of water, but a much smaller quantity of water will suffice if ether is used as a part of the solvent, and if potassium hydroxide is employed in place of sodium hydroxide. As the proportion of water increases, less benzoic acid, but more benzilic acid, results. Schönberg and Keller (A., 1923, i, 928) ascribe the formation of benzoic acid during the benzil rearrangement to oxidation by atmospheric oxygen, but it is shown that such an action does not occur. C. J. S.

Condensation of Benzoic Acid and Substituted Benzoic Acids with Resacetophenone. G. C. CHAKRAVARTI (*J. Amer. Chem. Soc.*, 1924, **46**, 682—685).—A number of dyes belonging to the benzein series have been prepared by heating, in presence of anhydrous zinc chloride, 2 mols. of resacetophenone with rather more than 1 mol. of benzoic or a substituted benzoic acid. The dyes show strong fluorescence in alkaline solution and yield colourless acetyl derivatives. Benzoic acid condensed with resacetophenone gives *resacetophenonebenzein* (annexed formula), forming rose-red crystals, m. p. 141°; *acetyl* derivative, m. p. 125°. *Resacetophenone-p-hydroxybenzein*, $C_{23}H_{18}O_6,4H_2O$, from *p*-hydroxybenzoic acid, has m. p. 107—108°, and when kept for several weeks is transformed into a "homochromo-isomeride," m. p. 192°; *acetyl* derivative, m. p. 102°. Salicylic acid yields a *benzein*, m. p. 133—135° (*acetyl* derivative, m. p. 128°). The *benzeins* obtained from anisic acid, *m*-bromobenzoic acid, and gallic acid have m. p. 161°, 147°, and 126°, respectively. Similarly constituted products of high m. p. are obtained from *m*- and *p*-nitro- and *p*-chlorobenzoic acids. C. J. S.



Constitution of Biochemically Formed Hydroxyketopropylbenzene. C. NEUBERG (*Biochem. Z.*, 1924, **144**, 44—46).—A reply to Auwers and Jordan (this vol., i, 384). It is pointed out that the structure ascribed by these authors to the β-ketol is in agreement with the views of Neuberg and Ohle, and that the exact constitution of the product formed by the action of carboligase in the presence of benzaldehyde is of little importance to the biological aspect of the activity of the enzyme. J. P.

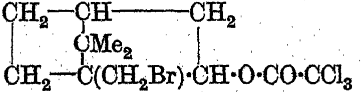
Functions of Chromophores. IX. The Quinone Chromophore. I. J. LIFSCHITZ, H. LOURIÉ, J. ZIMMERMANN, and G. A. TEN BOKKEL HUININK (*Rec. trav. chim.*, 1924, **43**, 269—282; cf. A., 1921, ii, 286, 287).—The absorption spectrum of *p*-benzoquinone in alcoholic solution consists of three bands with maxima at 2150 (A), 3400 (B), and 4400 (C). These bands may be assumed to correspond with the three groups of absorption bands of the vapour spectrum, and may therefore be attributed to different species of electrons or different groups of atoms. Substitution of the hydrogen atoms of *p*-benzoquinone by alkyl groups, as in toluquinone and *p*-xyloquinone, moves A without weakening it towards shorter wave-lengths, B and C in the opposite direction. Unsaturated hydrocarbon groups, as in anthraquinone, weaken A and strengthen B. Chlorine has a similar effect, but influences C irregularly. Chloranil owes its intense yellow colour to the broadening of B. Auxochromic groups having no residual valency, such as the ethoxy group, have a similar effect to chlorine, but intensified, whilst auxochromic groups having residual valency (·OH and ·NR$_2$) have such an extreme effect as to give the substance the character of a dyestuff. From the effect of chlorine on band A it is argued that this band is associated with the carbon atoms, since chlorine has the effect of weakening the conjugated system of the carbonyl groups and ethylenic linkings. This deduction is supported by the fact that A is strengthened and deepened in polynuclear quinones. Band B is attributed to the oxygen electrons, since the broadening of this band by alkyl groups and its shifting towards the red by halogens is similar to the effect of these radicals on the oxygen band of acetone. E. H. R.

Quinhydrone Salts. S. GOLDSCHMIDT and F. CHRISTMANN (*Ber.*, 1924, **57**, [*B*], 711—715).—The sodium salt of *p*-benzoquinhydrone, $C_6H_4O_2+C_6H_4O_2Na_2$, was obtained practically pure by treating a mixture of quinone and quinol with sodium ethoxide in dry ethereal solution; it formed a deep blue precipitate sufficiently stable, when dry, to be weighed in air. The blue *sodium salt* of o-*benzoquinhydrone* was obtained in a similar manner, in complete absence of air or moisture. Both salts are at once decomposed by water to give greenish-yellow or brown solutions respectively. The *sodium* salt of *phenanthraquinhydrone* was obtained as a deep green precipitate by dissolving phenanthraquinone in alcohol or pyridine, adding 10% sodium hydroxide and [illegible] sodium chloride solution, and then blowing in oxygen. It is practically insoluble in water in absence of air, but dissolves in pyridine to a deep green solution. The corresponding *barium* salt was also prepared. On treating a benzene solution of phenanthraquinol with lead dioxide, an emerald-green solution is obtained which is believed to contain a complex salt of the type ($xC_8H_{14}O_2+$ $yC_8H_{14}O_2Pb$). F. A. M.

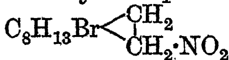
Direct Amination of Anthraquinone. J. KNIATOWNA (*Bull. Soc. chim.*, 1924, [iv], **35**, 207—211).—According to a German patent (D.R.-P. 287756), the product obtained by heating anthraquinone with hydroxylamine sulphate in concentrated sulphuric acid, in presence of ferrous sulphate for 2 hours at 180—190°, is practically pure 1-aminoanthraquinone. This claim cannot be substantiated. Only a very small portion of the product dissolves in hydrochloric acid, and the residue, after repeated crystallisation, gives anthraquinone. From the mother-liquors of these crystallisations molecular compounds of anthraquinone and aminoanthraquinone are obtained which melt between 253° and 271°. The formation of such compounds may be the cause of the contradictory values given in the literature for the melting point of 1-aminoanthraquinone. E. E. T.

Anthraquinonylsemicarbazides. M. BATTEGAY and P. DASSIGNY (*Bull. Soc. chim.*, 1924, [iv], **35**, 211—213).—Dianthraquinonylsemicarbazides are prepared by boiling together nitrobenzene solutions of β-anthraquinonylcarbamyl chloride and α- or β-anthraquinonylhydrazine. ββ'-*Dianthraquinonyl*-1:4-*semicarbazide*, $\beta\text{-}C_{14}H_7O_2\cdot NH\cdot NH\cdot CO\cdot NH\cdot\beta\text{-}C_{14}H_7O_2$, is an orange substance which turns orange-yellow at 300°, sublimes, and leaves a residue melting above 330°. αβ'-*Dianthraquinonyl*-1 : 4-*semicarbazide* is a reddish brown substance which turns orange at 270—275° and melts at about 310°. Both these compounds dye cotton from a hyposulphite vat, but the dyeings are irregular owing to partial decomposition taking place in the bath. E. E. T.

Constitution of so-called β-Bromocamphor. P. LIPP and F. LAUSBERG (*Annalen*, 1924, **436**, 274—286).—Although Wedekind, Schenk, and Stüsser have shown (A., 1923, i, 346) that Reychler's camphorsulphonic acid is an ω-derivative, the formation of "β"-bromocamphor from camphorsulphonyl bromide (*Chem. Soc. Proc.*, 1901, **17**, 244, 245) affords no proof of the ω-constitution of the bromocamphor owing to the possibility of isomeric change. The authors have accordingly attempted the preparation of "β"-bromocamphor from compounds containing the bromine atom in the ω-position. *d*-Camphene was converted into ω-bromocamphene, which by digestion with trichloroacetic acid at 40° yields the well-crystallised *trichloroacetate* (annexed formula), which was obtained in two stereoisomeric forms, m. p. 80° and 101—102°. On hydrolysis, the expected ω-bromo-borneol or -*iso*borneol was not obtained but by reduction with sodium amalgam in alcoholic solution the ester yields the α-campholen-



$$\begin{array}{lll} CH_2\text{—}CH & \text{———} & CH_2 \\ | \quad\quad CMe_2 & & | \\ CH_2\text{—}C(CH_2Br)\cdot & & CH\cdot O\cdot CO\cdot CCl_3 \end{array}$$

aldehyde of Ciamician and Silber (A., 1910, i, 496), b. p. 93·5—96°/19 mm. (*semicarbazone*, m. p. 160—162°). The aldehyde is easily resinified by alkalis and a resinous *substance*, $(C_{10}H_{16}O)_n$, b. p. 165—175°/4 mm., was isolated as a by-product in the reduction. On oxidation with nitric acid, *d*-ω-2-dibromocamphane gives an acid, $C_{10}H_{15}O_4Br$, m. p. 208—210°, an oily product containing nitrogen and halogen, which yields a yellow potassium salt, and a neutral substance, probably  $C_8H_{13}Br<\begin{matrix}CH_2\\ |\\ CH_2\cdot NO_2\end{matrix}$. The acid is identical with the "β"-bromocamphoric acid obtained by the oxidation of "β"-bromocamphor, the identity being confirmed by a comparison of the anhydrides. The m. p. of ω-bromocamphoric anhydride is given as 149—150° (cf. P., 1901, **17**, 244). *dl*-ω-2-Dibromocamphane similarly gives *dl*-ω-bromocamphoric acid (decomp. 208—210°), and the corresponding anhydride, m. p. 149—149·5°. For comparison *dl*-ω-camphorsulphonic acid was prepared from synthetic camphor by Reychler's method (A., 1899, i, 445) and from this, by Armstrong and Lowry's procedure, the *dl*-ω-bromocamphor, m. p. 76—77°, was obtained. On oxidation with nitric acid, this yields *dl*-ω-bromocamphoric acid, m. p. 210—211°, and anhydride, m. p. 149—150°, identical with the products obtained from *dl*-ω-2-dibromocamphane, and the authors accordingly assign the ω-structure to "β"-bromocamphor. R. B.

Optically Active Sulphilimines. F. G. Mann and W. J. Pope (*J. Chem. Soc.*, 1924, **125**, 911—918).—Attempts have been made to prepare sodium *d*-α-bromocamphor-π-sulphonchloroamide and by condensation with methyl ethyl sulphide to obtain the corresponding sulphilimine, $C_{10}H_{14}OBr\cdot SO_2N{:}SMeEt$, which, owing to the trihedral disposition of the three valencies of the doubly-linked nitrogen atom, should exist in two enantiomorphous forms. *d*-Bromocamphor-π-sulphonamide, on treatment with sodium hypochlorite, gives d-*bromocamphor-π-sulphondichloroamide*,

$$C_{10}H_{14}OBr\cdot SO_2\cdot NCl_2,$$

white crystals, m. p. 123—125°, which slowly lose chlorine on standing. No sodium or potassium salt could be obtained, and by treatment with alcoholic potassium hydroxide (either with or without ethyl sulphide) the dichloroamide yielded unchanged α-bromocamphor-π-sulphonamide and d-*α′-chloro-α-bromocamphor-π-sulphonamide*, $C_{10}H_{13}OClBr\cdot SO_2\cdot NH_2$, colourless needles, darkening at 225°, m. p. 232° (decomp.) (cf. Lapworth, T., 1899, 75, 558). For comparison, the d-*α-chloro-α′-bromocamphor-π-sulphonamide*, colourless needles, darkening at 224°, m. p. 232° (decomp.), was prepared by brominating ammonium *d*-α-chlorocamphor-π-sulphonate, treating the product with phosphorus pentachloride, yielding d-*α-chloro-α′-bromocamphor-π-sulphonyl chloride*, colourless crystals, m. p. 194—197° (effervescence), which with ammonia gives the sulphonamide. The two sulphonamides differ only in rotatory constants. d-*α-Bromocamphor-π-sulphonethylchloroamide*, $C_{10}H_{14}OBr\cdot SO_2\cdot NEtCl$, white crystals, m. p. 122—124° (efferv.), from *d*-α-bromocamphor-π-sulphonyl chloride and ethylamine is more stable than the dichloroamide, and can be crystallised from alcohol.

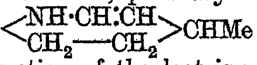
Sodium ethyl sulphide condenses with *d*-chloromethylenecamphor, giving *ethylthiolmethylene*-d-*camphor*, $C_{10}H_{14}O{:}CH\cdot SEt$, pale green liquid, b. p. 169—171°/17 mm., $d_{4^\circ}^{14\cdot 8}$ 1·0362. *Ethylthiolmethylene*-l-*camphor*, obtained similarly, is a pale green liquid, b. p. 168—169°/16 mm., $d_{4^\circ}^{15\cdot 0}$ 1·0357. Both sulphides condense with hydrated "chloramine-*T*" in boiling alcohol to give d- and l-*camphorylidene-methylethylsulphine*-p-*toluenesulphonylimine*,

$$C_{10}H_{14}O{:}CH\cdot SEt{:}N\cdot SO_2\cdot C_7H_7,$$

white crystals, m. p. 172° (efferv.). The rotatory powers of these sulphilimines are less than those of the parent substances, and no indication was obtained of the expected stereoisomerism. Rotatory powers are given for all the above compounds. R. B.

The Beckmann Rearrangement. X. S. Komatsu (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 147—150).—The author cites various examples of the Beckmann change and of nitrile formation, and points out that the latter reaction may be due to direct elimination of water from the oxime or to dehydration after the Beckmann change. C. J. S.

The Beckmann Rearrangement. XI. Catalytic Action of Reduced Copper on *l*-Menthoneoxime. S. Komatsu and M. Kurata (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 151—156).—When *l*-menthoneoxime and pure hydrogen were passed over reduced copper at 200°, the product contained menthone, dimenthylamine, *l*-menthylamine, *d*-menthylamine, menthonitrile, decenoic acid and its amide, and a basic substance, probably 4-methyl-7-*iso*propyl-*cyclo*hexenimine,



$Pr^{\beta}\cdot CH<\begin{matrix}NH\cdot CH{:}CH\\ CH_2\text{---}CH_2\end{matrix}>CHMe$ (cf. Wallach, A., 1903, i, 104). The production of the last is regarded as evidence of the momentary formation of menthone*iso*oxime, which undergoes the Beckmann rearrangement by catalytic action of the reduced copper. The menthonitrile and decenoic acid are supposed to be formed respectively by catalytic dehydration and hydration of decenamide. C. J. S.

Camphor Oils. I. Reaction between Camphor-red Oil and Sulphuric Acid. K. Ono (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 99—105).—According to Sugiyama (Japanese Pat. 37119, 1920), terpin hydrate is obtained when camphor-red oil is treated with sulphuric acid. The author shows that this result is due to the action of the acid on the terpineol present in the oil (cf. Aschan, A., 1919, i, 336) and gives the conditions to be employed in order to obtain the optimum yield of terpin hydrate. [Cf. *B.*, 1924, 447.] T. H. P.

Origin of Terpenes and Crystalline Acids in Pine Resins. G. Dupont (*Compt. rend.*, 1924, **178**, 1560—1562).—The hypothesis that the terpenes and resin acids in conifers have a common origin in a material secreted by the resin cells is developed. The secreted material, which has the formula $C_{10}H_{16}O$ (Köhler, A., 1912, i, 638), is converted by the action of a diastase into the terpene, $C_{10}H_{16}$, and the oxygen acting on two other molecules produces the resin acids, $3C_{10}H_{16}O=C_{10}H_{16}+C_{20}H_{30}O_2+H_2O$. This requires that the refined turpentine should contain 31% of the essential oil and 69% of resin acids, numbers which are in close agreement with the proportions actually found. The proportions of *d*- and *l*-pimaric acids and resin acids in the extract of the maritime pine, the fact that *d*-pimaric acid is found only in turpentines rich in nopinene, whilst the Aleppo pine, which yields only pinene, gives an extract containing alepic acid only, all support the hypothesis. J. W. B.

Eutectics of Camphene with other Terpenes. G. AUSTERWEIL (*Compt. rend.*, 1924, **178**, 1174—1175).—The separation of camphene from other terpenes (when the former is not present in excess of 30% of the mixture) by crystallisation at a low temperature is rendered impracticable by the formation of eutectic mixtures of low freezing point, which are comparatively rich in camphene. The melting points of a series of mixtures of camphene with α-pinene, β-pinene, mixtures of α- and β-pinene, and dipentene are given. H. J. E.

Melting Points of Mixtures of Camphene and Pinene. E. DARMOIS (*Compt. rend.*, 1924, **178**, 1546).—Austerweil's conclusion (preceding abstract) that French turpentine contains practically no camphene and that the low melting points of natural camphenes are explained by the presence of small quantities of impurities, was anticipated by the author (A., 1911, ii, 352). J. W. B.

Phellandrenes. II. H. G. SMITH, P. G. CARTER, and J. READ (*J. Chem. Soc.*, 1924, **125**, 930—940; cf. *ibid.*, 1923, **123**, 1657).—By solution in carbon disulphide, in which the α-nitrite is relatively insoluble, and fractional precipitation, the β-nitrite of *l*-α-phellandrene has been prepared from the essential oils of *Melaleuca acuminata*, *Eucalyptus dives*, and *E. phellandra* in a much higher state of purity than has hitherto been attained. The process of separation can only be controlled effectively by considering the melting points of the various fractions in association with the corresponding rotatory powers. The β-nitrite, m. p. 105—106°, is crystallographically indistinguishable from *l*-α-phellandrene α-nitrite, and has $[\alpha]_D^{20}$ −160° when freshly dissolved in chloroform, the values previously recorded being −36° (Schreiner, A., 1901, i, 600) and −40·82° (Wallach, A., 1904, i, 1035). The striking mutarotative changes of the β-nitrite in acetone, benzene, or chloroform solution, particularly in the presence of piperidine, are similar to those previously observed with the α-nitrite, but optical inversion only takes place in acetone solution. The α- and β-nitrites yield chemically and optically identical specimens of nitro-α-phellandrene and carvotanacetone ($\Delta^{5,6}$-menthen-3-one), and are thus both derived from *l*-α-phellandrene. It is probable that the low rotatory powers of the terpene fractions obtained from eucalyptus oils of the "peppermint group" are due to the presence of partly racemised *l*-α-phellandrene, and a similar remark applies to the essential oil of *Melaleuca acuminata*. R. B.

Oil of Turpentine extracted from the Firs of Bucovina. O. CZERNY (*Bul. Soc. Chim. România*, 1924, **6**, 39—41).—By submitting the greenish-yellow oil obtainable from the bark of the tree to distillation in a current of steam, an oil was obtained which after treatment with sodium hydroxide and subsequent distillation under diminished pressure, had b. p. 155—216°, d^{16} 0·875, $[\alpha]_D$ −39·2°, acid value 124, saponification value 107, esterification value 13. It was separated by fractional distillation into pinene, a mixture of sylvestrene and dipentene, an ester which on hydrolysis with alcoholic potassium hydroxide yielded borneol, and, probably, a sesquiterpene. The non-volatile residue from the steam distillation, amounting to some 75% of the total weight, was a hard, brittle solid, m. p. 55°, which on distillation yielded traces of acetic and succinic acids and a large amount of coloured oils of very low oxygen content. A. E. C.

Refractive Index of Gums. A. MALLOCK (*Nature*, 1924, **113**, 643).—A corrected table of refractive indices of certain organic solvent liquids and gums is given. A. A. E.

Method for obtaining Pure Glucosides Soluble in Water from Plants. S. GHOSH (*J. Amer. Pharm. Assoc.*, 1923, **12**, 1080—1081).—Steam is passed into an aqueous extract of the bark to which lead chloride and oxide have been added; lead remaining in solution after addition of sodium carbonate and filtration is removed with hydrogen sulphide. Sodium chloride can, if necessary, be removed from the product obtained on evaporation by recrystallisation from ethyl alcohol. CHEMICAL ABSTRACTS.

Nature of the Methyl Salicylate Glucoside present in the Bark of *Betula lenta*. M. BRIDEL (*Compt. rend.*, 1924, **178**, 1310—1312).—The glucoside isolated by Schneegans and Gerock (A., 1895, i, 109) from the bark of *Betula lenta* and named gaultherin yields, not merely methyl salicylate and dextrose, but also xylose, on hydrolysis. It is, indeed, identical with the author's monotropitin (A., 1923, i, 1275), and it is suggested that the latter name be retained and gaultherin discarded. T. H. P.

Biochemical Resolution of Rutin. Formation of a New Glucide, Rutinose. C. CHARAUX (*Compt. rend.*, 1924, **178**, 1312—1314).—The formation of rhamninose by the action of rhamninase on rutin (cf. Ter Meulen, A., 1911, i, 391) is questioned. From the defatted, dehusked seeds of *Rhamnus utilis* the author has obtained, by maceration with water followed by precipitation with alcohol, an enzyme which hydrolyses rutin with formation of quercetin and of a new sugar, termed *rutinose*. The latter is hygroscopic and has no sharp melting point, softening at about 140° and becoming liquid and darkening at 189—192°. It reduces Fehling's solution and exhibits mutarotation in aqueous, but not in alcoholic, solution. When hydrolysed by means of dilute hydrochloric acid, it yields rhamnose (1 mol.) and dextrose (1 mol.).

The same enzyme hydrolyses: robinin, giving a glucide composed of rhamnose (2 mols.) and galactose (1 mol.); a yellow glucoside

obtained from the flowers of *Spiræa ulmaria*, yielding a glucide (apparently different from rutinose), xanthorhamnin, primeverin, baptisin, helicin, and amygdalin. It is without action on *iso*-hesperidin.
T. H. P.

Plant Pigments. I. Yellow Colouring Matter of the Acacias. J. M. PETRIE (*Proc. Linnean Soc. N.S. Wales*, 1923, **48**, 356—367).—The soluble colouring matter of the yellow inflorescence of *Acacia discolor*, *A. linifolia*, *A. decurrens* (var. *mollis*), and *A. longifolia* is a rhamnose glucoside of kaempferol, fine, hair-like crystals. No free flavinol was found; the yellow flavinol (0·06%) on reduction with nascent hydrogen gave a red solution resembling that of the natural anthocyanilidine. Carotene and xanthophyll (0·14—0·3%) were present as plastid pigments. The tannins were composed of phloroglucinol, protocatechuic and gallic acids, and on hydrolysis gave red phlobaphen anhydrides.
CHEMICAL ABSTRACTS.

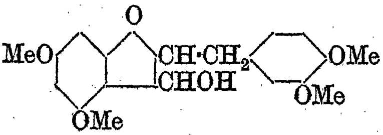
Insecticides. I. Isolation and Constitution of the Active Constituent of Dalmatian Insect Powder. H. STAUDINGER and L. RUZICKA.—(See i, 700.)

Electrolytic Reduction of Carbonyl Derivatives. H. HIBBERT and R. R. READ.—(See i, 613.)

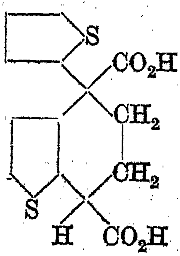
Humic Acids. H. TROPSCH and A. SCHELLENBERG.—(See i, 619—621.)

Degradation Product of Brazilin obtained by Schall and Dralle. P. PFEIFFER (*Ber.*, 1924, **57**, [*B*], 738; cf. this vol., i, **413**, **537**).—Tschitschibabin and Nikitin had already prepared 3-methoxychromanone from the corresponding methoxyphenoxypropionic acid.
F. A. M.

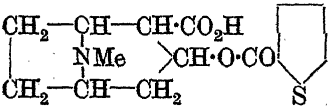
Tannins and Similar Substances. XV. A New Degradation of Catechin. K. FREUDENBERG, L. ORTHNER, and H. FIKENTSCHER (*Annalen*, 1924, **436**, 286—298).—The series of reactions which led to the elucidation of the structure of diacetonedextrose and -lævulose (A., 1923, i, 652) has now been applied to the case of catechin. By the action of toluene-*p*-sulphonyl chloride on tetramethyl-*d*-catechin in pyridine solution, the *p*-toluenesulphonic ester, $C_{26}H_{28}O_8S$, m. p. 87—88°, is obtained, which with hydrazine yields: (1) the primary *hydrazide*, $C_{19}H_{24}O_5N_2$ ($+H_2O$, lost *in vacuo* at 65°), m. p. 101—104°, this substance being oxidised by potassium permanganate to give a little tetramethyl-*d*-catechin, m. p. 145°. (2) The highly unstable 3-*mp*-dimethoxyphenylpyrazoline, m. p. 144—145° (*picrolonate*, m. p. 207—208°), which on oxidation with potassium permanganate yields veratric acid, demethylation with hydriodic acid giving a *substance* having m. p. about 240°. (3) Phloroglucinol dimethyl ether, identified as the dibromotrimethyl ether and as *phenacylphloroglucinol dimethyl ether*, m. p. 89°. The condensation of veratraldehyde with acetaldehyde in alcoholic potassium hydroxide gives 3 : 4-*dimethoxycinnamaldehyde*, bright yellow, rhombic crystals, m. p. 82—83°, which with hydrazine affords the above 3-*mp*-dimethoxyphenylpyrazoline. The constitution favoured for tetramethylcatechin is that represented by the annexed formula, although two other possibilities are discussed. Dichloropentacetyl-*d*-catechin (*Ber.*, 1880, **13**, 694), when treated with methyl sulphate and methyl-alcoholic potassium hydroxide, affords *dichlorotetramethyl*-d-*catechin*, long, white needles, m. p. 156—157°. R. B.



Thiophen Series. XVIII. Synthesis of the "Thiophen-isologue" of Atropine. W. Steinkopf and A. Wolfram (*Annalen*, 1924, **437**, 22—36).—Ethyl thienyl-2-glyoxylate (b. p. 138—140°/13 mm.) was prepared by treating thiophen with ethyl oxalic chloride (cf. Scholl and Egerer, A., 1913, i, 588) in presence of aluminium chloride. With magnesium methyl bromide, it gives *ethyl α-hydroxy-α-2-thienylpropionate*, an oil, b. p. 134—135°/13 mm., readily hydrolysed by barium hydroxide to the corresponding *acid*, needles, m. p. 107°. When alkali hydroxide is used as hydrolysing agent, side reactions take place and an amorphous product resembling that described below is obtained. It was found impossible to isolate α-2-thienylacrylic acid; the above hydroxy-acid, treated with acid in various ways, gives solely a mixture of two *isomerides*, one amorphous (decomp. 95°), the other crystalline, m. p. 216°. The latter, termed di-α-thienylacrylic acid, has properties which suggest that it has the annexed formula. The amorphous substance was also obtained as a by-product in the preparation of β-*chloro-α-2-thienylpropionic acid*, which was eventually isolated by treating α-hydroxy-α-2-thienylpropionic acid with hydrogen chloride in ether solution at −40° to −30°. It forms rhombs, m. p. 77°. Hydrolysed with calcium carbonate, it gives β-*hydroxy-α-2-thienylpropionic acid*, prisms, m. p. 95·5—96°, the *acetyl* derivative of which is oily, and when treated with thionyl chloride yields β-*acetoxy-α-2-thienylpropionyl chloride*, also an oil. Tropine with the latter compound in benzene solution affords β-*hydroxy-α-2-thienylpropionyltropine*, "*thiophen-cocaine*" (*chloroplatinate*, decomp. 240—241°, and *picrate*, m. p. about 142°, described). The quantity obtained was insufficient for pharmacological tests. W. A. S.

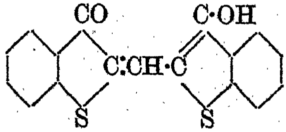


Thiophen Series. XVII. Preparation of the "Thiophen-isologue" of Cocaine. W. Steinkopf and W. Ohse (*Annalen*, 1924, **437**, 14—22).—"Thiophen-cocaine" was obtained by methylating the product of interaction of ecgonine and thiophen-2-carboxylic anhydride. Thiophen-2-carboxylic acid is best prepared (yield: 96%) from 2-bromothiophen (Steinkopf, A., 1923, i, 124) by the Grignard reaction (cf. Schlenk and Ochs, A., 1915, i, 579). The best yield (62%) of 2-cyanothiophen, the intermediate in an alternative preparation of the acid, was obtained when cyanogen chloride was used; the bromide, iodide, and cyanogen itself gave poor yields (cf. Karrer and others, A., 1919, i, 591). Thiophen-2-carboxylic acid heated with acetic anhydride yields the *anhydride*, needles, m. p. 62° b. p. 218—220°/15 mm., rapidly reacting in warm aqueous suspension with ecgonine to give *thiophen-2-carboxyecgonine* (annexed formula), which sinters at 94°, solidifies and melts at 186°, and has $[\alpha]_D^{17\cdot5}$ —19·07° to —17·49° in chloroform. Its *hydrochloride* has m. p. 225° (decomp.). The *methyl* ester, viz. "*thiophen-cocaine*," has m. p. 107°; its *hydrochloride*, m. p. 184·5°, the *picrate*, yellow needles, m. p. 175°, and *chloroplatinate* are described. Pharmacologically the substance closely resembles cocaine but appears to be less toxic. W. A. S.

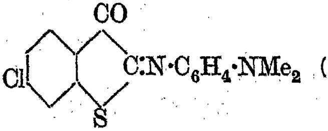


Fission of Indigoid Dyes by Alkalis. P. FRIEDLÄNDER and L. SANDER (*Ber.*, 1924, 57, [*B*], 648—652; cf. A., 1922, i, 764).—Thioindigotin when heated with 45% potassium hydroxide and a little alcohol is converted into oxythionaphthen, thionaphthenquinone, and a little of the known substance (I). 6 : 6′-Dichlorothioindigotin is much more resistant to the above treatment and affords 6-chloro-3-oxy(1)thionaphthen (colourless needles, m. p. 143°) (cf. Ruppel, *Dissert.* Darmstadt, 1921), and *6-chlorothionaphthenquinone.* The latter (orange needles, m. p. 134°) was also prepared by condensing the chloro-oxythionaphthen with *p*-nitrosodimethylaniline, the resulting *6-chlorothionaphthenquinone*-p-*dimethylamino-2-anil* (II) (dark green, metallic prisms, m. p. 190°) being hydrolysed by hydrochloric acid. 6 : 6′-Dichloro-4 : 4′-dimethylthioindigotin, on treatment with alkali, gives only a trace of 6-*chloro*-4-*methylthionaphthenquinone*, orange needles, m. p. 132°, which was also prepared from the *anil*, m. p. 123·5°. *iso*Indigotin has been prepared by an improved method (due to B. Homolka) from isatin and an aqueous solution of sodium sulphide and ammonia. It is converted by hot aqueous-alcoholic sodium hydroxide into *hydroxydihydroisoindigotin*, (III), colourless leaflets or needles, m. p. 250—280° (decomp.) (converted by hot acetic anhydride into diacetyl*iso*indigotin), and *quinindolinecarboxylic acid* (IV), yellow needles (*sodium* salt, $C_{16}H_9O_2N_2Na,3H_2O$, yellow needles), a little isatin and other substances also being formed. The acid, when heated at 300°, affords quinindoline (cf. Gabriel and Eschenbach, A.,

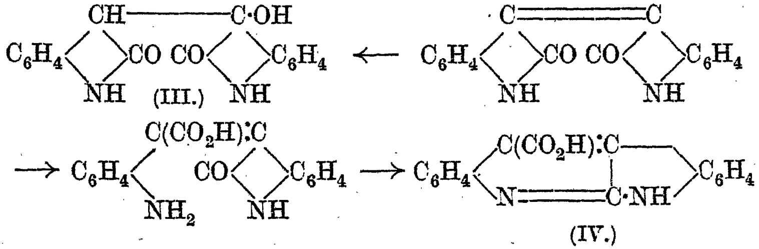
(I.)



(II.)



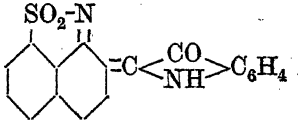
1898, i, 199). The decomposition by alkali probably occurs as shown below:

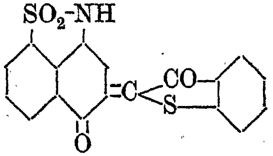


F. A. M.

Indigoid Dyes. P. FRIEDLÄNDER and L. SANDER (*Ber.*, 1924, **57**, [*B*], 637—648).—The following new indigoid dyes are described: the *dye* (I) from naphthasultam and isatinanilide by condensation in presence of acetic anhydride, forms deep bluish-violet needles with red iridescence which give a yellow solution in alkali.

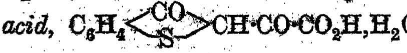
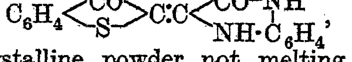
(I.)





(II.)

The condensation of 3-oxy(1)thionaphthen with naphthasultamquinone in acetic acid yields a *dye* (II) which forms purple-black needles. No dye could be obtained on attempting to condense isatinanilide with the *p*-tolylsulphamide of α-naphthylamine, although the latter couples with diazo compounds in alkaline solutions. A re-examination of the "2-dihydronaphthalene-2′-indoleindigo" described by Herzog and Kreidl (A., 1923, i, 61) showed that their product was probably an impure "2-naphthalene-2-indoleindigo." The substance described by Herzog and Kreidl as 1-keto-2 : 3′-oxy-2′-thionaphthentetrahydronaphthalene may, however, have the structure ascribed to it, although analysis alone is insufficient to determine the presence or absence of the two hydrogen atoms; on warming with concentrated aqueous-alcoholic sodium hydroxide, it forms a yellow solution from which acetic acid precipitates a yellow, amorphous *additive* compound with water possibly $C_{10}H_8O{:}C(OH){\cdot}CO{\cdot}C_6H_4{\cdot}SH$. Above 100°, the dye is re-formed; the hydrated compound behaves like an enol and like a mercaptan. 6-*Ethoxythionaphthenquinone*-2-*anil* was prepared from 6-ethoxythionaphthen and nitrosobenzene as yellow needles, m. p. 118—119°. It condensed with α-ketotetrahydronaphthalene in acetic anhydride to give the brownish-red dye, "3 : 4-*dihydro*-2-*naphthalene*-6′-*ethoxy*-2′-*thionaphthenindigo*." 2-*Chloro*-1 : 4 *naphthaquinone monoanil* was obtained by condensing 2-chloro-α-naphthol with nitrosobenzene in presence of ammonia as fiery red needles, m. p. 112°; it was not possible to obtain an indigoid dye from it by condensation with oxythionaphthen; by using sodium hydroxide in the above condensation in place of ammonia, the product was almost entirely Euler's anilinonaphthaquinone-monoanil, the chlorine atom being removed. The following *acyl* derivatives of indigoid dyes were also prepared: "N-*Acetyl-2-indole-2′-thionaphthenindigo*," from the corresponding indigoid dye, acetic anhydride, and acetyl chloride, forms light red needles; *di*(N-*acetyl*)iso*indigotin*, obtained similarly from *iso*indigotin, forms brick-red crystals. N : N′-*bis*(*chloroacetyl*)*indigotin* was obtained from indigotin and chloroacetyl chloride as ruby-red, quadratic, double pyramids; it is sensitive to water-vapour and gradually becomes coated with indigotin; "4-*acetylamino-2-naphthalene-2′-indoleindigo*" is a violet-blue product, and "4-*acetylamino-2-naphthalene-2′-thionaphthenindigo*" reddish-violet. Treatment of indigotin with oxalyl chloride in boiling nitrobenzene afforded *oxalylindigotin* as yellow needles, m. p. above 200°. It is extremely easily hydrolysed by dilute alkali with regeneration of indigotin and is sulphonated by warm fuming acid (20% SO_3). These observations confirm Friedländer's view (A., 1922, i, 765) that saturation of the nitrogen atoms in indigoid dyes leads to lightening of the colour. F. A. M.

Derivatives of 3-Oxy(1)thionaphthen. L. R. HART and S. SMILES (*J. Chem. Soc.*, 1924, **125**, 876—881).—*o*-Thiolbenzoic acid condenses with compounds containing a labile methylene group to give 3-oxythionaphthen derivatives (cf. T., 1923, **123**, 2907), but in no case are 2 : 2-disubstituted derivatives formed; one of the groups originally attached to the methylene group is always displaced, and if this cannot happen the reaction does not take place. *o*-Thiolbenzoic acid and oxalacetic, acetylpyruvic, or pyruvic acid react in sulphuric acid solution to give 3-*oxy*(1)*thionaphthen-2-glyoxylic acid*,  $C_8H_4{<}\genfrac{}{}{0pt}{}{CO}{S}{>}CH\cdot CO\cdot CO_2H,H_2O$, m. p. 174° when anhydrous. The *calcium* salt is described. The *phenylhydrazone* forms orange needles, m. p. 187°, and the *anil* yellow plates, m. p. 190°. The o-*amino-anil* forms yellow prisms (converted into the following compound before melting). When *o*-phenylenediamine and the acid were mixed in boiling acetic acid, "2-*thionaphthen-2-quinoxalineindigo*,"  $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{S}{>}C{:}C{<}\genfrac{}{}{0pt}{}{CO-NH}{NH\cdot C_6H_4}$, was readily formed as a red, crystalline powder not melting below 315°. 2-*Benzoyl-3-oxy*(1)*thionaphthen* was produced by condensation of *o*-thiolbenzoic acid and benzoylacetone; it forms orange or pale yellow needles, m. p. 116—117°. Its *phenylhydrazone* crystallises in orange plates, m. p. 160°. Its acetyl derivative, 2-*benzoyl-3-acetoxy*(1)*thionaphthen*, forms needles, m. p. 106°. 2-*Acetyl-3-benzoyloxy*(1)*thionaphthen*, formed by benzoylating 2-acetyl-3-oxythionaphthen, has m. p. 145°. The disinclination to form 2 : 2-disubstituted derivatives is again shown here. 2-*Benzoyl-3-benzoyloxy*(1)*thionaphthen* crystallises in plates, m. p. 113°.

W. A. S.

Constitution of Evodiamine and Rutæcarpine. Y. Asahina (*J. Pharm. Soc. Japan*, 1924, No. 503, 1—7; cf. Asahina and Mayeda, A., 1921, i, 48).—Indole-β-ethylamine (3-aminoethylindole) is obtained by the decomposition of evodiamine. The constitutions of evodiamine and rutæcarpine are, therefore, as stated by Kermack, Perkin, and Robinson (T., 1921, **119**, 1615).

K. K.

Methylation of Tertiary Amines and Alkaloids by means of Methyl Sulphonic Esters derived from Phenols. L. J. Simon and M. Frèrejacque (*Compt. rend.*, 1924, **178**, 945—947).—When treated with methyl iodide or sulphate or with one of various sulphonic esters derived from aromatic hydrocarbons, hexamethylenetetramine yields the salt of a quaternary methylated base, one methyl group being fixed by a tertiary nitrogen atom: $C_6H_{12}N_4+R\cdot OMe=C_6H_{12}N_3(NMe)\cdot OR\longrightarrow C_6H_{12}N_3\cdot NMe\cdot OH$. This reaction is effected very readily and completely by the methyl sulphonates derived from phenols (A., 1923, i, 462, 1098), giving the phenolsulphonates of the same base. The reaction is best carried out in chloroform solution and, even in the cold, is extremely sensitive, 0·02 g. of hexamethylenetetramine rapidly yielding the characteristic crystalline compounds. The *compounds* obtained, with their approximate decomposition temperatures, are as follows: $OH\cdot C_6H_4\cdot SO_3Me$ [1 : 4], 225°; $OH\cdot C_6H_3Me\cdot SO_3Me$ [2 : 1 : 5], 134°; $OH\cdot C_6H_3Me\cdot SO_3Me$ [OH : Me=1 : 4], 175°; $OMe\cdot C_6H_4\cdot SO_3Me$ [1 : 4], 195°; $OMe\cdot C_6H_3Me\cdot SO_3Me$ [2 : 1 : 5], 190°; $OMe\cdot C_6H_3Me\cdot SO_3Me$ [OMe : Me=1 : 4], 215°; $OH\cdot C_6H_3(CO_2Me)\cdot SO_3Me$ [OH : CO_2Me=2 : 1], 230°. These salts yield the corresponding *picrates* when treated with picric acid in aqueous solution.

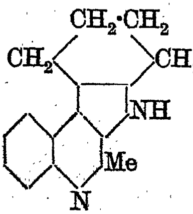
Compounds of similar type are obtainable from antipyrine, pyramidone, dimethylaniline, and pyridine, a solvent other than chloroform being sometimes necessary. The products obtained from antipyrine by means of the methyl sulphonates of methyl salicylate and anisole have m. p. 135° and 96°, respectively. The salt formed from pyramidone and methyl anisolesulphonate has m. p. 162°, and that from pyramidone and dimethyl sulphosalicylate, m. p. 97°. The reaction is applicable also to the alkaloids. T. H. P.

Kinetics of Catalytic Dehydrogenation. II. N. Zelinsky and G. Pawlow (*Ber.*, 1924, **57**, [*B*], 669—671; cf. A., 1923, i, 767).—Palladium is a much more active catalyst than platinum in effecting the dehydrogenation of piperidine, which, with the first metal, only follows a normal course at temperatures below 250°; at higher temperatures the catalyst becomes partly inactivated owing to subsidiary reactions. The phenomenon is due to the chemical nature of piperidine, since the dehydrogenation of *cyclo*hexane (*loc. cit.*) occurs normally within much wider limits of temperature. With piperidine, as with *cyclo*hexane, dehydrogenation commences at about 150°; between 150° and 200°, piperidine is much more energetically dehydrogenated by palladium than is *cyclo*hexane.

H. W.

Spectrochemistry of Heterocyclic Nitrogen Compounds. K. VON AUWERS and W. KOHLHAAS (*Annalen*, 1924, **437**, 36—63).—Densities and refractivities for the α, He, β, and γ lines at various temperatures are recorded for pyrrole, 1-methylpyrrole, 2 : 4- and 2 : 5-dimethylpyrroles, and 2 : 3 : 5-trimethylpyrrole; for 26 pyrazole compounds, including 3 : 5-*dimethylpyrazole*, m. p. 58° (*picrate*, m. p. 153°); 4-*chloro*-1-*phenyl*-3 : 5-*dimethylpyrazole*, b. p. 162—165°/10—11 mm.; for 20 derivatives of tetrahydroindazole (cf. this vol., i, 325) and for 21 of indazole itself (cf. also A., 1921, ii, 73; 1922, ii, 98). W. A. S.

Mechanism of E. Fischer's Synthesis of Indoles. Application of the Method to the Preparation of a Pyrindole Derivative. G. M. ROBINSON and R. ROBINSON (*J. Chem. Soc.*, 1924, **125**, 827—840).—Largely polemical against Hollins (A., 1922, i, 863). Reddelien's explanation of the reaction (A., 1912, i, 263), involving as it does an oxidation and scission of the hydrazone as an intermediate stage, is untenable because, in the first place, tetrahydrocarbazole may be obtained from *cyclo*hexanonephenylhydrazone even when stannous chloride is present in the reaction mixture, and, secondly, 2-methylindole, or nitrotetrahydrocarbazole, is produced normally even when *p*-toluidine, or aniline, respectively, is added to supply, on Reddelien's hypothesis, an alternative base. Further, *N*-methyltetrahydrocarbazole is the sole product of the action of hot acetic acid and aniline (20 mols.) on *cyclo*hexanonephenylmethylhydrazone. Thus the authors' original theory (A., 1918, i, 448) is substantiated. The same general method has been applied to the synthesis of a pyrindole derivative (cf. Fargher and Furness, A., 1915, i, 842). 3-*Hydrazinoquinaldine*, prepared by reducing diazotised 3-aminoquinaldine, first with sodium hydrogen sulphite, then with the hyposulphite, forms pale yellow needles, m. p. 169°. *Benzaldehydequinaldyl*-3-*hydrazone* crystallises in yellow plates, m. p. 202°, its *hydrochloride* in needles, m. p. 261°. *cyclo*Hexanonequinaldyl-3-hydrazone has m. p. about 100° in the crude (colourless) condition, but when recrystallised is converted into an orange *dioxide*(?), needles, m. p. 131° (decomp.). This yields 3-quinaldineazo-β-naphthol when fused with β-naphthol and generally behaves remarkably like quinaldine-3-diazo-4-oxide (Conrad and Limpach, A., 1888, 1109). By treating quinaldylhydrazine with a large excess of *cyclo*hexanone, 3-*methylbenzo*-(5 : 6-)9 : 10 : 11 : 12-*tetrahydro*-4-*carboline* (annexed formula) was obtained. This substance crystallises from benzene in needles, m. p. 198°, containing benzene (1 mol.), which is lost at 140—150°, the substance then melting at 226°. Its *methosulphate* has m. p. 225°; treated with potassium hydroxide, it yields 3 : 4-*dimethylbenzo*-(5 : 6-)9 : 10 : 11 : 12-*tetrahydro*-4-*isocarboline*, yellow needles, m. p. 120° (decomp.). *cyclo*Hexanone interacts with hydrazine itself to form an azine (cf. Mailhe, A., 1922, i, 332), which with zinc chloride forms a *compound*,



$C_{12}H_{20}N_2,HCl,ZnCl_2$, colourless prisms, m. p. 271—272°. Certain analytical figures relating to the compound obtained from cotarnine and 6-nitropiperonal are corrected (cf. T., 1914, **105**, 1468).

W. A. S.

Intramolecular Condensation Reactions of Aminoaldehydes and Aminoacetals. II. Course of the Reaction in the Formation of Dihydroquinoline and a New Preparation of Indole Derivatives. C. Räth (*Ber.*, 1924, **57**, [*B*], 715—718; cf. this vol., i, 555).—When *o*-aminopropylbenzene is heated with chloroacetal at 250° the expected *4-ethyl*-1 : *2-dihydroquinoline*, a pale yellow oil (b. p. 125—135°) with slightly tarry odour (*hydrochloride*, pinkish, hygroscopic, and amorphous), is formed together with *3-ethoxy-4-ethyl*-1 : 2 : 3 : *4-tetrahydroquinoline*, a yellow, viscous oil (b. p. 180—185°/21 mm., or 175—185°/17 mm.). β-Chloropropionacetal and aniline when heated together at 250° give a little dihydroquinoline and (mainly) *4-ethoxytetrahydroquinoline*, a yellowish-brown, viscous oil (b. p. 264—270°), which darkens in air (*picrate*, fine, yellow needles). *3-Ethoxy*-1-*ethyl*-2 : *3-dihydroindole* (*hydrochloride*, amorphous), a thick, yellow liquid, b. p. 153—163°/11 mm., is obtained from ethylaniline and bromoacetal, although the chief product in this case is 1-ethylindole.

F. A. M.

Synthesis of 2 : 4 : 7- and 2 : 4 : 8-Trimethylquinolines. S. Yamaguchi (*J. Pharm. Soc. Japan*, 1924, No. 503, 8—33).—The author has synthesised 2 : 4 : 7- and 2 : 4 : 8-trimethylquinolines and their salts, from acetone, paraldehyde, and *m*- and *o*-toluidines, respectively. Generally speaking, 2 : 4 : 6- and 2 : 4 : 7- but not 2 : 4 : 8-derivatives have a large affinity for water and for methyl iodide.

2 : 4 : 8-Trimethylquinoline is a white solid, m. p. 42°, b. p. 269—270°, and gives the following salts: *hydrochloride*, m. p. 238°; *hydrobromide*, m. p. 251° (decomp.); *hydriodide*, m. p. 224°; *chloroaurate*, m. p. 191°; *chloroplatinate*, m. p. 275° (decomp.); *mercurichloride*, m. p. 234°; *zincichloride*, m. p. 295—296° (decomp.); *hydrogen sulphate*, m. p. 263°; *dichromate*, decomp. at about 180°; *picrate*, m. p. 193°; methiodide, m. p. 229° (decomp.).

2 : 4 : 7-Trimethylquinoline is a colourless, oily liquid, b. p. 280—281°, d^{20} 1·0337, n_D^{24} 1·59732. On exposure to air, or when crystallised from water, it forms a crystalline *hydrate*, m. p. 48°. The following salts are described: *hydrochloride*, sublimes at about 310°; hydrobromide, m. p. 351° (decomp.); *hydriodide*, m. p. 320° (decomp.); *chloroaurate*, m. p. 152°; *chloroplatinate*, m. p. 272° (decomp.); *mercurichloride*, m. p. 244°; *zincichloride*, m. p. 258°; *hydrogen sulphate*, m. p. 223°; *dichromate*, decomp. at about 179—180°; *picrate*, decomp. 232°; methiodide, subliming at about 322°.

K. K.

Relations between Chemical Constitution and Taste. (Miss) C. Riccomanni (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 145—148).—1 : 4-Di-δ-phenyl-Δ^β-pentenoylpiperazine, prepared by heating piperazine at 100—105° with δ-phenyl-Δ^β-pentenoic acid (cf.

Staudinger and Schneider, A., 1923, i, 361; Staudinger and Müller, A., 1923, i, 363), is obtained as a dense, brownish-yellow oil with a pungent, aromatic taste, yields a yellow *picrate*, m. p. 245°, and when mixed in the proportion of 2% with flour produces a taste similar to, although less intense than, that of pepper. Evidently piperidine is not necessary for obtaining the flavour of pepper.

When added in the proportion of 1% to flour, styryl methyl ketone exhibits a markedly sharp taste (cf. Nomura, T., 1917, i, 769; A., 1918, i, 446; Nomura and Nozawa, A., 1918, i, 438); cinnamylidenemethyl methyl ketone has an intense, biting taste which appears after a time; benzyl methyl ketone has also an acute taste and acetophenone a pungent taste which disappears almost immediately. With compounds which lack the phenyl group or which contain a partly hydrogenated aromatic ring, such as ionone, the acute taste disappears almost completely.

2-Acetylpyrrole, 2-pyrryl styryl ketone, and the product of the condensation of cinnamaldehyde with 2-acetylpyrrole,

$$C_4H_4N{\cdot}CO{\cdot}CH{:}CH{\cdot}CH{:}CHPh,$$

have sweet, and in no way pungent, tastes. T. H. P.

Preparation of New Salts of CC-Disubstituted Barbituric Acids. E. LAYRAUD (Brit. Pat. 202660).—New salts are obtained by mixing hot aqueous solutions of *as*-CC-disubstituted barbituric acids and piperazine. *Piperazine ethylbutylbarbiturate* melts at about 150—155°. The piperazine salts (acid : base=1 : 1 mol.) afford stable aqueous solutions. *Salts* are also obtained by treating ethyl*iso*butyl-, ethyl*iso*amyl-, propylbutyl-, propyl*iso*butyl-, and propyl*iso*amyl-barbituric acids with either an organic base, other than piperazine, or an inorganic base, other than sodium.

W. T. K. B.

Synthetic Hypnotics of the Barbituric Acid Series. A. W. DOX (*J. Amer. Pharm. Assoc.*, 1923, **12**, 602—609).—A consideration of the nature of the group producing hypnotic effect. In the veronal class, the group $\cdot CR_2{\cdot}CO{\cdot}NH{\cdot}CO\cdot$ is a "hypnophore." Macht's "specific benzyl effect" is simply a higher alcohol effect. To manifest hypnotic action without undesirable after-effects, the two 5-alkyl groups of the pyrimidine ring should together contain between 4 and 8 carbon atoms; at least one such group must be of open-chain form. The benzyl group is undesirable, the carbamide group may not be replaced by the amidine group, and the molecular weight should not exceed about 250. CHEMICAL ABSTRACTS.

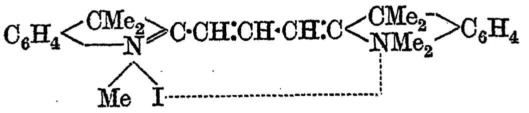
Hypnotic and Analgesic Compounds from Dimethylaminophenyldimethylpyrazolone and Dialkylbarbituric Acids. E. H. VOLWILER (U.S. Pat. 1478463).—Yellow or orange-yellow, crystalline compounds, m. p. 94·5—96·5°, 88—90°, 84—86°, and 90—94°, are produced from dibutyl-, ethylbutyl-, ethyl*sec.*butyl-, and ethyl*iso*amyl-barbituric acids, respectively. *Ethyl*sec.*butylbarbituric acid* is obtained by condensing ethyl ethyl*sec.*butylmalonate (b. p. 133°/48 mm.) with carbamide in the presence of sodium ethoxide. CHEMICAL ABSTRACTS.

Mother Substance of Indian-yellow. F. MAYER (*Arch. Exp. Path. Pharm.*, 1924, **101**, 383—385).—The formulæ proposed by Wiechowski (A., 1923, i, 591) for mangin and euxanthone are at variance with the accepted conclusions of Fischer and Piloty (A., 1891, i, 677) and other workers; they are therefore to be regarded as erroneous. W. O. K.

Constitution of Pyrazoles, Indazoles, and Anthranils. K. VON AUWERS (*Annalen*, 1924, **437**, 63—86).—A discussion of the bearing of data previously obtained (see i, 666) on the constitution of these compounds. To assist in calculating atomic refractivities for singly-linked or doubly-linked nitrogen, refractivity measurements were made on eleven substituted hydrazines, whilst the constants for five more indazole derivatives, anthranil itself, and three substituted anthranils are also recorded. The author's conclusion is that none of the indazole compounds contains a 3-membered ring structure and that the 1- and 2-derivatives differ only in the arrangement of the double bonds. Anthranil and related compounds should be formulated as analogous to indazole, not as internal amides. W. A. S.

Sulphonation of Glyoxalines. II. R. FORSYTH, J. A. MOORE, and F. L. PYMAN (*J. Chem. Soc.*, 1924, **125**, 919—923).—Attempts to remove the methyl group from 2-methylglyoxaline-4-sulphonic acid so as to determine the constitution of glyoxalinesulphonic acid (T., 1920, **117**, 1429) failed. Oxidising agents either did not act or completely disrupted the molecule. A benzylidene compound was not formed. When glyoxaline is treated with 70% oleum at 160° for 36 hours the product contains 15% of a *disulphonic acid*. 2-Methylglyoxaline, similarly treated for 3—6 hours, gives 2-*methylglyoxaline*-4-*sulphonic acid*, $C_4H_5N_2\cdot SO_3H,H_2O$, prisms, m. p. (decomp.) about 279° when anhydrous. The *ammonium*, *barium*, and *sodium* salts are described. In some experiments, a small proportion (up to 17%) of the 4 : 5-*disulphonic acid* was produced. This forms needles containing $1\cdot 5H_2O$ and has m. p. 280°; its *barium* salt is described. Neither glyoxalinesulphonic acid nor methylglyoxalinesulphonic acid afforded esters or chlorides. Partial hydrolysis took place when they were heated at 170° with concentrated hydrochloric acid. Treated with bromine (1 mol.) in aqueous solution, glyoxalinesulphonic acid gives ammonium bromide, oxalic acid, and 2 : 4 : 5-tribromoglyoxaline, 65% of the acid being recovered unchanged; methylglyoxalinesulphonic acid behaves similarly, yielding a little 4 : 5-dibromo-2-methylglyoxaline and 4-bromo-2-methylglyoxaline-5-sulphonic acid (cf. Light and Pyman, T., 1922, **121**, 2626). W. A. S.

Indoleninocyanines [Indocyanines]. W. KÖNIG [with E. WAGNER] (*Ber.*, 1924, **57**, [*B*], 685—692; cf. A., 1923, i, 1188). —1 : 2 : 3 : 3-Tetramethylindolenium iodide is converted by ethyl orthoformate in boiling acetic anhydride solution into 1 : 3 : 3 : 1′ : 3′ : 3′-*hexamethyl*strepto*monovinylene*-2 : 2′-*indocyanine iodide* (annexed formula), golden needles, m. p. about 229° (decomp.).



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CMe_2}{N}{>}C\cdot CH{:}CH\cdot CH{:}C{<}\genfrac{}{}{0pt}{}{CMe_2}{NMe_2}{>}C_6H_4 \quad \overset{N}{\genfrac{}{}{0pt}{}{\diagup\ \diagdown}{Me\quad I}}$$

The corresponding *bromide*, m. p. 250° (decomp.), *chloride*, decomp. 250°, *perchlorate*, m. p. 245° (decomp.), and *picrate*, m. p. 205°, are described. The new dye is remarkable among quinocyanines on account of its relatively great stability towards mineral acids and light. It is converted by a very large excess of sodium hydroxide into the corresponding pale yellow *ψ-base*, m. p. about 96° (decomp.), which when suspended in water passes into equilibrium with the red onium base. 5-*Chloro*-1 : 2 : 3 : 3-*tetramethylindolenium iodide*, pale yellow needles, m. p. 198°, prepared by fusing acetone-*p*-chlorophenylhydrazone with zinc chloride, is converted in a similar manner into 5 : 5′-*dichloro*-1 : 3 : 3 : 1′ : 3′ : 3′-*hexamethyl*strepto*monovinylene*-2 : 2′-*indocyanine iodide*, needles, m. p. 265°; the corresponding *carbinol base*, a pale yellow, amorphous substance, has m. p. about 130° (decomp.).

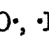
H. W.

Preparation of Diaminodiaryldialkylmethanes. FARBW. VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 204722).—Aniline, or a nuclear alkyl-substituted derivative with a free *p*-position, is caused to react, in the form of a salt in aqueous solution, with an aliphatic ketone (*e.g.*, by heating under pressure at 120—150°). pp′-*Diaminodiphenyldimethylmethane*, $CMe_2(C_6H_4\cdot NH_2)_2$, forms colourless needles, m. p. 132°. pp′-*Diaminodi*-m-*tolyldimethylmethane* (from *o*-toluidine and acetone) has m. p. 71°, and pp′-*diaminodiphenylmethylethylmethane* (from aniline and methyl ethyl ketone), m. p. 78°. These compounds are valuable as intermediates for dyes.

W. T. K. B.

Dyes derived from Carbazole and Thiodiphenylamine. S. DUTT (*J. Chem. Soc.*, 1924, **125**, 802—807).—Carbazole condenses with aldehydes and ketones in presence of concentrated sulphuric acid or zinc chloride to form triarylmethane compounds which may be oxidised to dyes. As 3-nitro-, but not 3 : 6-dinitro-, carbazole will so condense it is inferred that substitution takes place in position 3. With formaldehyde the *compound*, $CH_2(C_{12}H_8N)_2$, colourless needles, m. p. 287°, is obtained; benzaldehyde affords the *leuco*-base, $CHPh(C_{12}H_8N)_2$, needles, m. p. above 300°, which, oxidised with nitrosyl chloride in sulphuric acid solution, gives the dark green *chloride* of the dye, the colourless *carbinol base* of which is obtained by boiling with pyridine and forms needles, m. p. above 290°. Similar compounds were prepared using *p*-dimethylaminobenzaldehyde [dark violet needles; *carbinol base*, m. p. 282° (decomp.)], *m*-nitro- and *m*-chloro-benzaldehydes. When sulphonated, all these products dye unmordanted cotton in green to violet shades. Benzophenone, *pp*′-tetramethyldiaminobenzophenone, and 2 : 3 : 4-trihydroxybenzophenone yield (with phosphoryl chloride as condensing agent) *compounds* of the type, $C_{12}H_8N\cdot CPh_2Cl$. The *carbinol base* of the first named forms colourless needles, m. p. 172°, and its *chloride* violet needles, m. p. 280—285°; the remainder have m. p.

above 290°. All dye wool in violet shades and the last-named dyes chrome-mordanted textiles dark violet or black shades. Thiodiphenylamine yields analogous derivatives. With oxalic acid, a green *compound*, $C(C_{12}H_8NS)_3\cdot CO_2H$, giving a colourless *base*, $C(C_{12}H_8NS)_3\cdot OH$, m. p. 225—227°, was formed. Benzaldehyde (*carbinol base*, decomp. 200°) and *p*-dimethylaminobenzaldehyde gave compounds dyeing cotton green and grey, respectively, from a sulphide bath. *p*-Hydroxy- and *m*-nitro-benzaldehydes also condense. With benzophenone, and its 2 : 3 : 4-trihydroxy and *pp'*-tetramethyldiamino derivatives, compounds were produced which dye wool or unmordanted cotton blue or violet shades. These substances are decomposed by concentrated sulphuric acid. Thiodiphenylamine will also condense with nitrosophenols (*p*-nitrosophenol, *p*-nitroso-*m*-dimethylaminophenol, dinitrosoresorcinol, α-nitroso-β-naphthol, β-nitroso-α-naphthol), giving products which, unlike the carbazole-indophenols, will dye cotton from a hyposulphite or sulphide "vat." By fusion with sodium polysulphide at 250—300°, they yield sulphur dyes giving green, brown, or black shades. Compounds with similar properties are formed with diketones (benzil, phenanthraquinone, isatin). W. A. S.

Preparation of Acylacetyl Compounds. CHEM. FABR. GRIESHEIM-ELEKTRON (Brit. Pat. 211772).—Diacylacetyl compounds are prepared by heating, preferably in a solvent (*e.g.*, a benzene hydrocarbon, chlorobenzene, nitrobenzene, naphthalene, or a large excess of the acylacetic ester used), at least 2 mols. of an acylacetic ester with 1 mol. of a diamine of the general formula $NH_2\cdot Y\cdot NH_2$, where Y represents an aryl or substituted aryl residue, a diaryl or substituted diaryl residue, or a residue of a diaryl compound of the type $-Ar\cdot Z\cdot Ar'-$, where Ar and Ar' stand for the same or different aryl or substituted aryl residues united by a connecting link, Z, which may be $\cdot O\cdot$, $\cdot S\cdot$, $\cdot CH_2\cdot$, $\cdot CO\cdot$, $\cdot NH\cdot$, $\cdot NHCO\cdot$, $\cdot N{:}N\cdot$,  $O<\begin{matrix}N\cdot\\ |\\ N\cdot\end{matrix}$, $\cdot NH\cdot CO\cdot NH\cdot$, $\cdot O\cdot CH_2\cdot CH_2\cdot O\cdot$, or the like. The diacylacetyl compounds have a substantive character, so that they can be fixed on the cotton fibre in alkaline solution and developed with diazo compounds, giving shades which are fast to washing. Details of the preparation of several representatives are given, and the following new compounds described. *Diacetoacetyl*-p-*phenylenediamine*: slender, colourless needles, m. p. 167° (decomp.); *diacetoacetyl*-o-*tolidine*: slender, lustrous needles, m. p. 204—205° (decomp.); *diacetoacetyl*-o-*dianisidine*: feebly yellow needles, m. p. 164—165° (decomp.); *dibenzoylacetyl*-o-*tolidine*: slender, colourless, lustrous needles, m. p. 233° (decomp.); *diacetoacetyl*-4 : 4'-*diaminobenzophenone*: colourless, lustrous needles, m. p. 175—176° (decomp.); *diacetoacetyl*-4 : 4'-*diaminoazobenzene*: orange-yellow, crystalline powder, decomp. 233—234°; *diacetoacetyl*-1 : 4-*naphthylenediamine*: colourless needles, m. p. 197° (decomp.); *diacetoacetyl*-1 : 5-*naphthylenediamine*: silvery scales, m. p. 249—250° (decomp.); *diacetoacetyl*-2 : 6-*naphthylenediamine*: lustrous needles, m. p. 203—204° (decomp.); *diacetoacetyl*-o : o'-*dichloro*-

benzidine: colourless, crystalline flocks, decomp. 145—147°; *diacetoacetyl*-m : m′-*dichlorobenzidine*: colourless needles, decomp. 212°; *dibenzoylacetylbenzidine*: yellow, crystalline powder, m. p. 248° (decomp.); *diacetoacetyl*-4 : 4′-*diamino*-3 : 3′-*dichlorodiphenylmethane*: colourless, small crystals, m. p. 138—139° (decomp.); *diacetoacetyl*-4 : 4′-*diamino*-3 : 3′-*ditolylmethane*: colourless, felted needles, m. p. 143—144° (decomp.); *diacetoacetyl*-4 : 4′-*diaminoazoxybenzene*: brownish-yellow, crystalline powder, m. p. 219—220° (decomp.); *diacetoacetyl*-4 : 4′-*diamino*-3 : 3′-*azotoluene*: bright yellow powder, m. p. 215° (decomp.); *diacetoacetyl*-4 : 4′-*diaminodiphenylcarbamide*: colourless, lustrous leaflets, melting above 320°.
W. T. K. B.

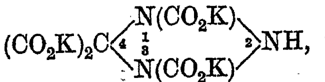
Preparation of [Azo] Dyestuffs derived from Pyrazolone and of Intermediate Products therefor. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 210669).—1-Aryl-5-pyrazolones are prepared by condensing the hydrazine derivative of an aromatic primary amine containing a sulphonamido group (*e.g.*, 3-aminobenzene-1-sulphonamide) with a suitable derivative of a β-ketonic acid (*e.g.*, ethyl acetoacetate or ethyl oxaloacetate). By coupling these pyrazolones with a diazo compound, azo dyes are obtained which are remarkable for their uniformity and purity of tint (yellow to red). More particularly is this the case with the mordant dyes obtained by coupling the new pyrazolones with diazo derivatives of *o*-aminophenol and *o*-aminonaphthol, and especially with the acid dyes containing chromium produced by treating these mordant dyes with a chroming agent (*e.g.*, chromium formate). [Cf. *B.*, 1924, 412.]
W. T. K. B.

Scission of Disulphides. Synthesis of Triazoles. E. FROMM, L. BRÜCK, R. RUNKEL, and E. MAYER (*Annalen*, 1924, **437**, 106—124).—A continuation of earlier work (cf. A., 1922, i, 377; Arndt and others, A., 1921, i, 813; 1922, i, 277, 375). 5-Amino-3-phenylamino-1 : 2 : 4-triazole has m. p. 163°, not 77° or 157°, as previously given. It forms a *benzylidene* compound, yellow needles, m. p. 225°, and a *tribenzoyl* derivative, yellow crystals, m. p. 126°. 3-Phenylamino-5-thiol-1 : 2 : 4-triazole may be oxidised to the corresponding disulphide which, treated with hot 25% sodium hydroxide, gives an equimolecular mixture (cf. *pp*′-dinitrodiphenyldisulphide, Fromm and Wittmann, A., 1908, i, 631) of the parent thioltriazole and 3-*phenylamino*-1 : 2 : 4-*triazole*, m. p. 180°, yielding a *dibenzoyl* derivative, m. p. 111—112°. 3-p-*Tolylamino-5-thiol*-1 : 2 : 4-*triazole*, from *p*-tolyldithiobiuret and hydrazine hydrate, forms colourless crystals, m. p. 271°; its *dibenzoyl* derivative, yellow leaflets, has m. p. 129°, and the *benzyl*(*thio*)*ether*, needles, m. p. 182°; this also yields a *benzoyl* derivative, scales, m. p. 133°. 5-*Amino*-3-p-*tolylamino*-1 : 2 : 4-*triazole*, the subsidiary product of the above reaction, has m. p. 178—180°, its *benzylidene* derivative, m. p. 219°. The thioltriazole, oxidised with ferric chloride, yields the *disulphide*, a yellow powder, m. p. 229°, which, treated with sodium hydroxide, gives, as above, 3-p-*tolylamino*-1 : 2 : 4-*triazole*, m. p. 199°, the *benzoyl* derivative of which forms yellow leaflets, m. p. 172°. Similar compounds containing the *o*-tolyl and *o*-anisyl radicals were prepared. *Cyano*-o-*tolylcarbamide* has m. p. 65—68°; 3-o-*tolylamino*-5-*thiol*-1 : 2 : 4-*triazole* forms needles, m. p. 263°; its *dibenzoyl* derivative has m. p. 133°, the *benzyl*(*thio*)*ether*, m. p. 161°, and this also yields a *dibenzoyl* derivative, leaflets, m. p. 125°. 5-*Amino*-3-o-*tolylamino*-1 : 2 : 4-*triazole* has m. p. 165°, and easily decomposes; its *hydrochloride* forms needles, m. p. 187°, the *benzoyl* derivative, scales, m. p. 220°. o-*Tolylthiocarbamide* has m. p. 158°; the corresponding *triazole disulphide* forms a yellow powder, m. p. 277°. o-*Anisyldithiobiuret*, m. p. 148°, treated with iodine, gives o-*anisylthiuret hydriodide*, m. p. 200°, and with benzyl chloride a *compound*, m. p. 130°. 3-o-*Anisylamino*-5-*thiol*-1 : 2 : 4-*triazole* has m. p. 280°; its *benzyl*(*thio*)*ether*, m. p. 108°; its *dibenzoyl* derivative forms yellow scales, m. p. 138°. *Aminoguanidino*-o-*anisylthiocarbamide* crystallises in needles, m. p. 134—135°, its *hydrochloride* has m. p. 178—180°, and its *benzylidene* compound forms pale yellow scales. 5-*Amino*-3-p-*phenetylamino*-1 : 2 : 4-*triazole* has m. p. 191°, its *dibenzoyl* derivative, a yellow substance, melts at 176°, and its *diacetyl* derivative at 168°. 3-p-*Phenetylamino*-5-*thiol*-1 : 2 : 4-*triazole* has m. p. 268°, its *dibenzoyl* compound, m. p. 145°, its *benzyl*(*thio*)*ether* forms needles, m. p. 172°, and yields a *benzoyl* derivative, yellow needles, m. p. 122°. The corresponding *disulphide* is an amorphous powder convertible, as above, into 3-p-*phenetylamino*-1 : 2 : 4-*triazole*, m. p. 185°. 5-*Amino*-3-*ethylphenylamino*-1 : 2 : 4-*triazole* forms scales, m. p. 198°; its *benzoyl* derivative, yellow crystals, has m. p. 188·5°, its *acetyl* derivative m. p. 157°. The corresponding 5-*thioltriazole* forms needles, m. p. 127°, *dibenzoyl* derivative, m. p. 118°, *benzyl*(*thio*)*ether*, m. p. 94°, and the *benzoyl* derivative of the latter, m. p. 65°. The by-product of the hydrazine hydrate reaction here is 3-amino-5-thiol-1 : 2 : 4-triazole (cf. Fromm and Arndt, *loc. cit.*), ethylaniline being split off. This triazole yields a 1 : 4-*dibenzoyl* derivative, m. p. 178°. The *benzoyl* derivative of 5-*benzoylamido*-3-*thiol*-1 : 2 : 4-*triazole* has m. p. above 260°.

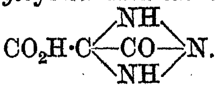
W. A. S.

Derivatives of *cyclo*Triazobutane [*cyclo*Triazomethene]. O. Diels and H. Behncke (*Ber.*, 1924, **57**, [*B*], 653—656).—The formation of additive products from azodicarboxylic ester and compounds containing an "acidic" methylene group is described (cf. A., 1923, i, 391, and previous abstracts).

Ethyl azodicarboxylate reacts with ethyl cyanoacetate in the presence of potassium acetate at 60° to form the *compound*, $CO_2Et\cdot C(CN):[N(CO_2Et)\cdot NH\cdot CO_2Et]_2$, an unstable, yellow liquid, b. p. 150—155°/0·4 mm. Ethyl malonate reacts with ethyl azodicarboxylate to yield the *substance*, $(CO_2Et)_2C[N(CO_2Et)\cdot NHCO_2Et]_2$, colourless, prismatic plates, m. p. 107°, which is remarkably stable towards acids and oxidising agents, and with methyl azodicarboxylate gives the corresponding *methyl* ester, m. p. 140—141°. Either ester is transformed by methyl-alcoholic potassium hydroxide solution into *potassium* cyclo*triazomethene*-1 : 3 : 4 : 4-*tetracarboxylate*,



$(CO_2K)_2C\left<\begin{matrix}N(CO_2K)\\ N(CO_2K)\end{matrix}\right>NH$, which could not be freed completely from potassium carbonate, but is converted by acetic acid into *potassium hydrogen* cyclo*triazomethene*-4 : 4-*dicarboxylate*, pyramids, m. p. 287° (decomp.). The latter salt with sulphuric acid affords cyclo*triazomethene*-4 : 4-*dicarboxylic acid* (long prisms, m. p. 237°, after softening and decomposing at 218°), which passes in a vacuum at 100° into 2 : 4-*carbonyl*cyclo*triazomethene*-4-*carboxylic acid*,



$$CO_2H\cdot C\left<\begin{matrix}NH\\ -CO-\\ NH\end{matrix}\right>N.$$

The monocarboxylic acid loses carbon dioxide at 218°, to give 2 : 4-*carbonyl*cyclo*triazomethene*, colourless prisms, m. p. 237°.
H. W.

Action of Pyridine on Hydrazono-acid Chlorides. C. Bülow and F. Seidel (*Ber.*, 1924, **57**, [*B*], 629—633).—The compound [m. p. 186°, not 168°, as erroneously recorded by Bülow and Neber (A., 1913, i, 999)] obtained from 2 : 4-dichlorophenylhydrazinopyruvyl chloride and pyridine is shown to have the constitution, $CH_3\cdot CO\cdot C(C_5H_4N):N\cdot NH\cdot C_6H_3Cl_2$, since the basic properties of the pyridine nitrogen atom are retained in it, as is proved by the formation of a *hydrochloride*, m. p. 168°, a *chloroaurate*, and a *chloroplatinate*. Similarly, the pentabromo derivative obtained from 4-phenylazo-3-methylisoxazolone (Hecking, *Diss.*, Tübingen, 1913) or from ethyl phenylazoacetoacetate (Memminger, *Diss.*, Tübingen, 1910) is transformed by cold pyridine into the *compound*,

$$CH_3\cdot CO\cdot CH(C_5H_4N)\cdot NBr\cdot NBr\cdot C_6H_3Br_2,$$

red needles, m. p. 162° (*hydrochloride*, m. p. 159—160°), which is converted by zinc and alcoholic hydrochloric acid into pyridine and *p*-bromoaniline. The composition $C_{15}H_{13}ON_3Br_4$ is assigned to the product of the action of pyridine on the pentabromo compound from 4-*o*-tolylazo-3-methylisoxazolone (Memminger, *loc. cit.*). The 2 : 4-dichlorophenylhydrazone of ethyl α-chloroglyoxylate is transformed by pyridine into the *substance* $C_{15}H_{14}O_2N_3Cl_3,H_2O$, yellow crystals, m. p. 142° after darkening at 130°.
H. W.

Colour of Azo Compounds and their Salts. F. Kehrmann and S. Hempel (*Ber.*, 1924, **57**, [*B*], 751; cf. A., 1917, i, 593).—An acknowledgment of the priority of V. Piccard (A., 1913, i, 895), regarding the colours of 4 : 4′-diaminoazobenzene, its tetramethyl derivative, and their salts in different solvents.
F. A. M.

Indoleazobenzene. W. Madelung (*Ber.*, 1924, **57**, [*B*], 751; cf. this vol., i, 423).—An acknowledgment of the preparation by Pieroni [*Atti R. Accad. Lincei*, 1921, (v), **30**, i, 267] of indoleazobenzene.
F. A. M.

Preparation of Acylacetyl Compounds. Chem. Fabr. Griesheim-Elektron (Brit. Pat. 211814).—Acylacetyl compounds are obtained, under exactly similar conditions to those required in the preparation of diacylacetyl compounds (cf. Chem. Fabr.

Griesheim-Elektron, this vol., i, 671), by the interaction of an acylacetic ester and a monoamine of the general formula $NH_2{\cdot}R{\cdot}X{\cdot}R'$, where R represents an aryl residue, R′ the same or a different aryl residue or a heterocyclic or acyclic residue containing a methylene group capable of coupling with diazo compounds, X an azo or azoxy group, or the residue of a 5-membered heterocyclic nucleus. The products resemble the diacylacetyl compounds in their substantive character. The following compounds are described. *Acetoacetyldehydrothiotoluidine*: colourless, crystalline powder, m. p. 170—172° (decomp.); *acetoacetylbenzeneazo*-1-*naphthylamine*: slender, orange needles, m. p. 154—155° (decomp.); *acetoacetyl*-4-*aminoazobenzene*: yellowish-orange, finely-crystallised powder, m. p. 130—131°; *acetoacetyl*-4′-*aminobenzeneazo*-1-*phenyl*-3-*methyl*-5-*pyrazolone*: slender, orange-yellow, lustrous needles, decomp. 208°; *acetoacetyl*-o-*aminoazotoluene*: slender, orange-yellow needles, m. p. 147°; *acetoacetyl*-m-*aminoazotoluene*: orange, opalescent scales, m. p. 133—134°; *acetoacetyl*-4′-*chloro*-4-*aminoazobenzene*: slender, orange-yellow, felted needles, m. p. 188°; *acetoacetyl*-3′-*nitro*-4-*aminoazobenzene*: slender, orange-yellow, felted needles, m. p. 138° (decomp.); *acetoacetyl*-4′-*nitro*-4-*aminoazobenzene*: orange-red, lustrous scales, m. p. 190—191° (decomp.); *acetoacetyl*-4-*aminoazoxybenzene*: small, pale yellow rods, m. p. 138° (decomp.); *acetoacetyl*-4′-*amino*-2′-*methylbenzeneazo*-2-*naphthalene*: orange-yellow, spherical aggregates, m. p. 153—154°; *acetoacetyl*-4′-*aminobenzeneazo*-p-*cresol*: clusters of orange-yellow needles, m. p. 165°. W. T. K. B.

Dimorphism of Diphenylarsenious Chloride (Diphenylchloroarsine). C. S. Gibson and D. C. Vining (*J. Chem. Soc.*, 1924, **125**, 909—911).—Diphenylarsenious chloride (b. p. 178·6°/10 mm.) crystallises in two forms. The unstable modification, obtained by spontaneous crystallisation of freshly redistilled material, or by heating the stable form at 130° and cooling under "aseptic" conditions, forms needles, m. p. 18·2—18·4°, whilst the stable modification forms rhombic, biaxial crystals, m. p. 38·7—38·9°. [Cf. T., 1920, **117**, 777, 1447.] W. A. S.

Organo Derivatives of Bismuth. VII. Iodo and Nitro Derivatives of Triphenylbismuthine. J. F. Wilkinson and F. Challenger (*J. Chem. Soc.*, 1924, **125**, 854—864).—The red substance obtained by Challenger and Allpress (T., 1915, **107**, 17) consists mainly of phenyldi-iodobismuthine. *Triphenylbismuthine di-iodide*, Ph_3BiI_2, seems to be formed by direct union of triphenylbismuthine and iodine in ether solution at —78°, but decomposes at the ordinary temperature, giving the red solid. Triphenylbismuthine reacts with cyanogen bromide at 120°, giving diphenylbromobismuthine, bismuth oxybromide, and benzonitrile, whilst with cyanogen chloride scarcely any action takes place. This is in remarkable contrast to the action with cyanogen iodide (Challenger and Allpress, *loc. cit.*). Triphenylstibine and cyanogen iodide yield, presumably by interaction with moisture, in cold ether solution, *triphenylstibine hydroxyiodide*, $Ph_3Sb(OH)I$, m. p. 196°; triphenylarsine and triphenylphosphine gave, with the same reagent, what appeared to be similar additive compounds which decomposed on contact with water (cf. Steinkopf and others, A., 1922, i, 72). A nitric–sulphuric acid mixture at −15°, or fuming nitric acid at its melting point, completely disrupts triphenylbismuthine, giving *m*-dinitrobenzene as the organic product; with benzoyl nitrate, however, a *dinitrate*, $Ph_3Bi(O\cdot NO_2)_2$, was obtained; *tri*-p-*chlorophenylbismuthine dinitrate*, m. p. 163—165°, was obtained in a similar way. Triphenylbismuthine dinitrate is converted by cold nitric acid (*d* 1·52), into, according to conditions, a *mononitro* derivative, convertible into an unstable *dichloride*, m. p. 105—110°; a *dinitro* derivative, yielding a *dichloride*, m. p. 136° (decomp.); a *tetranitro* derivative, convertible into the dichloride, m. p. 146°, which when heated until it decomposes gives *m*-chloronitrobenzene, the presumption being therefore that one nitro group in the bismuthine is in the meta-position (cf. Gillmeister, A., 1898, i, 138). *Tetranitrotriphenylbismuthine dihydroxide* was also obtained as an insoluble yellow powder, m. p. 108° (decomp.); boiled with alcohol it gives trinitrotriphenylbismuthine(?). Lastly, *hexanitrotriphenylbismuthine dinitrate* was obtained and converted into a *dichloride*, m. p. 148—149°. W. A. S.

Action of Inorganic Halides on Organo-metallic Compounds. F. CHALLENGER and F. PRITCHARD (*J. Chem. Soc.*, 1924, **125**, 864—875).—A general discussion of earlier work (T., 1922, **121**, 104; cf. also Goddard and others, *ibid.*, 1923, **123**, 1163, etc.) and the following new observations. *Tri-α-naphthylstibine*, m. p. 218°, from antimony trichloride and magnesium α-naphthyl bromide, gives a *dichloride*, m. p. 260°, and a yellow *dibromide*, m. p. 229° (decomp.). *Tri*-m-*tolylbismuthine dibromide* has m. p. 92°. Although tri-*m*-tolylarsine may be obtained in a similar way from the appropriate Grignard reagent, *tri*-m-*tolylstibine hydroxychloride*, m. p. 209°, was the only product obtained by treating antimony trichloride with magnesium *m*-tolyl bromide. Triphenylstibine and phosphorus trichloride interact in the cold to give mainly triphenylstibine dichloride; triphenylarsine only reacts with the same reagent at 160°, and then incompletely, yielding diphenylchloroarsine; triphenylphosphine gives the dichloride and decomposition products. Arsenic trichloride and triphenylstibine at 80° yield triphenylstibine dichloride and a little arsenic. Antimony trichloride and triphenylarsine form an additive *compound*, m. p. 78°. The same reagent with triphenylphosphine produces a similar *compound*, m. p. 96°. Triphenylphosphine forms analogous compounds with arsenic trichloride [product has m. p. about 100° (decomp.) and a little arsenic separated] and with bismuth chloride (m. p. 100—105°). The latter, heated at 270° and treated with water, gave metallic bismuth and triphenylphosphine oxide. Triphenylbismuthine and stannic chloride also form an additive compound. Triphenyl-bismuthine and -stibine react to some extent with silicon tetrachloride, giving diphenylchlorobismuthine and triphenylstibine dichloride, respectively; triphenylarsine does not react. Titanium tetrachloride and triphenylbismuthine form a red compound and eventually yield diphenylchlorobismuthine; triphenylstibine gives only the dichloride, whilst triphenylarsine gives an unstable additive product. Attempts to prepare organic titanium compounds by interaction of titanium tetrachloride and magnesium phenyl bromide failed. W. A. S.

Fractionation of Gelatin by Extraction with Alcohol and Precipitation with Aluminium Hydroxide and Barium Chloride. M. A. Rakusin (*Chem.-Ztg.*, 1924, **48**, 249—250).—A sample of commercial "*Gelatina albissima*" was extracted with 95% alcohol, and the extract and the residue were investigated by precipitation with 10% aluminium hydroxide, the filtrate being precipitated with barium chloride. The various fractions were tested by the biuret, Ostromisslenski, and Molisch reactions, and and the composition of the gelatin is given as follows: free amino compounds, 0·50%; free carbohydrates, 0·96%; biuret complex, 49·27%; combined carbohydrates, 23·77%; combined chondroitin–sulphuric acid, 25·50%. The distribution of the mineral matter (3·29%) is uncertain. All the sulphur present in gelatin is combined in the form of chondroitin–sulphuric acid, which contains 5·71% of sulphur. Gelatin is therefore not an individual chemical substance, and gelatins obtained from different raw materials may have different properties. H. C. R.

Gelatin-sulphuric Acid and Casein-sulphuric Acid. J. Hatano (*Biochem. Z.*, 1924, **145**, 182—185).—By the action on gelatin and casein, in the presence of pyridine, of chlorosulphonic acid dissolved in dry chloroform, stable sulphates of these proteins are obtained. The preparation of gelatin sulphate obtained contained 1·7% of sulphur against 0·35% in the original gelatin, whilst casein sulphate preparations contained 0·84% and 1·38% of sulphur as compared with 0·62% in the original protein. J. P.

Products of Prolonged Tryptic Digestion of Casein. S. Fränkel, H. Gallia, A. Liebster, and S. Rosen (*Biochem. Z.*, 1924, **145**, 225—241).—After prolonged hydrolysis (2 months) of casein, the following products have been isolated: *d*-tyrosine anhydride, *d*-tryptophan anhydride, *d*-leucine anhydride, and histidine anhydride. The first three dextrorotatory anhydrides are supposed to arise from the lævorotatory amino-acids by the successive actions of the enzymes waldenase—bringing about an optical inversion—and anhydrase. In addition *d*-alanine, *d*-glutamic acid, *l*-oxyproline, *l*-serine, and *d*-valine were obtained, in part as such, and in part as the racemic forms. *l*-Proline, $[\alpha]_D^{12}$ $-74{\cdot}08°$ in water, *d*-*iso*leucine, $[\alpha]_D^{12}$ $+12{\cdot}77°$ in water, and *l*-aspartic acid were isolated in the unchanged condition, whilst glycine was partly converted into methylamine by the action of a decarboxylase. In the course of such prolonged hydrolysis, leucine is converted into the anhydride whilst *iso*leucine remains unchanged (cf. also A., 1922, i, 184; 1923, i, 398). J. P.

Protein Coagulation in Drops. IV. Influence of the Nature of the Proteins and Precipitants on the Precipitate. L. Cikánek, J. Havlík, and F. Kubánek (*Biochem. Z.*, 1924, **145**, 98—103).—The influence of a large number of substances on the coagulation of serum proteins has been studied, using the Bečka drop method. The presence in the precipitant of halogens, hydroxyl, sulphonyl, and nitro groups increases the precipitating action, whilst amino groups lower it. The precipitating powers of the aliphatic alcohols decrease with increase in the number of hydroxyl groups. With certain solutions of sodium sulphide, potassium hydroxide, and potassium cyanide, the albumin, but not the globulin, fraction is precipitated, whilst the reverse result is obtained with solutions of copper sulphate, cadmium nitrate, aluminium chloride, and disodium hydrogen phosphate. Certain pathological horse sera show a characteristic behaviour on precipitation with ferrous sulphate, pyrogallol, and tannin. J. P.

Influence of Hydrolysis on the Capacity of Proteins to Bind Acids and Bases. T. B. Robertson (*Austral. J. Exp. Biol.*, 1924, **1**, 31—37).—The ratio, equivalents of acid or base bound/equivalents of free amino-nitrogen, has been determined for casein and gelatin before and after hydrolysis by trypsin at p_H 2·0, 8·2, and 10·5. Except for gelatin at p_H 10·5, the ratio decreases as a result of hydrolysis. It is concluded, therefore, that the predominant method of union of proteins with acids and bases is through internal –CO·NH– groups rather than through free amino or carbonyl groups. O. O.

Halogenated Proteins. I. Bromo-ovalbumin. A. J. J. Vandevelde (*Rec. trav. chim.*, 1924, **43**, 158—162).—The action of bromine dissolved in carbon tetrachloride on some proteins in the form of a dry powder afforded bromo derivatives of higher halogen content than previously recorded. This is stated to be due to the fact that secondary reactions brought about by the presence of water were obviated. The following bromo derivatives (hygroscopic, orange-coloured powders of penetrating odour) are described: *Bromo-ovoprotein A*, soluble in water, yielding a strongly acid solution in which 87·1% of the total bromine is in the form of hydrobromic acid. At 100°, the substance loses hydrogen bromide to give *bromo-ovoprotein C*, which also yields an acid solution. Its colour, however, prevents it being examined with a coloured indicator. On dissolving the first-named substance in *N*-sodium hydroxide and then acidifying with acetic acid, a precipitate of *bromo-ovoprotein S* is formed. The percentages of bromine in these three substances are 37·5, 31·48, and 4·73, respectively. H. J. E.

Protein Phytotoxins, with Special Reference to the New "Modeccin." H. H. Green and P. Kamerman (*J. S. Afr. Chem. Inst.*, 1924, **7**, 3—5).—The roots of *Modecca digitata* (more correctly, *Adenia digitata*) contain a highly poisonous phytotoxin to which the name *modeccin* has been given; the fatal dose is

0·0005 mg. per kg. of body-weight, when injected intravenously or subcutaneously. In its general properties the substance resembles the other known phytotoxins, namely, ricin (from *Ricinus communis*), abrin (from *Abrus precatorius*), crotin (from *Croton tiglium*), robin (from *Robinia pseudacacia*), and curcin (from *Jatropha curcus*); all are stable up to about 70°, but destroyed rapidly at 100°. They are insoluble in 60% alcohol and are precipitated by ammonium sulphate and other salts. Modeccin resists hydrolysis by pepsin or trypsin for 3 days at 37°, but is destroyed by trypsin in 14 days; it does not possess hæmagglutinative properties and in this respect differs from ricin. W. P. S.

Protein Studies. III. Decomposition of Silk Fibroin by Fermentation. F. WESSELY.—(See i, 696.)

Biochemistry.

Effect of Salts of Calcium, Sodium, and Potassium on Respiratory Exchanges. I. Effect of Parenteral Administration of these Salts. W. ARNOLDI and J. FERBER (*Z. klin. Med.*, 1923, **97**, 208—216; from *Chem. Zentr.*, 1924, i, 494).—Injection of salts of calcium, sodium, and potassium produced increased utilisation of oxygen and diminution in respiratory quotient and the output of carbon dioxide in humans. Respiration within the tissues was increased. G. W. R.

Catalytic Action of Blood. L. WALLING and O. O. STOLAND (*Amer. J. Physiol.*, 1923, **66**, 503—518).—Blood catalase is accurately determined by reaction at p_H 8·9, 22°, for 0·5 hour; it is destroyed above 47° and is only slightly affected at 0°. In acid hydrogen peroxide at 22° it is apparently destroyed and its action complete in 10 minutes; with optimum alkalinity it acts for 3 hours or more. Sodium chloride (0·9%) in acid hydrogen peroxide increases, and in alkaline retards, the catalytic effect of blood.
CHEMICAL ABSTRACTS.

Influence of Rarefied Air on the Gaseous Metabolism of the Blood. A. LOEWY and J. FÖRSTER (*Biochem. Z.*, 1924, **145**, 318—323).—The blood of rabbits which had been kept under diminished pressure (430—460 mm.) for 24 to 33 hours showed a greater oxygen consumption than that of normal rabbits. The average figures found per 100 c.c. of blood per hour were 5·272 c.c. in the former and 2·733 c.c. in the latter case. J. P.

Cell Volume and Electrical Conductivity of Blood. H. C. GRAM (*J. Biol. Chem.*, 1924, **59**, 33—40).—The conductivity of whole blood and of serum, and the cell volume, were measured. An empirical curve has been obtained from which the cell volu may be read, if the ratio of the conductivity of the whole blood to that of the serum is known. W. O. K.

Rarefied Air and Blood Regeneration by "Hæmopoietins." J. Förster (*Biochem. Z.*, 1924, **145**, 309—317).—Serum from rabbits which had been kept in atmospheres at a pressure of 410 to 480 mm. for 1—2 days injected into rabbits rendered anæmic by bleeding, produced an increase in the rate at which the number of the red blood-corpuscles returned to the normal value. Normal sera and the proteins of milk did not produce this effect, which is ascribed to the production in the bone marrow, under the stimulus of the diminished pressure, of active substances—" hæmopoietins " (Carnot and Deflandre, *Compt. rend.*, 1906, **143**, 384)—which then find their way into the blood-stream. J. P.

Ultrafiltration of Blood Serum and Cerebrospinal Fluid. G. Egerer-Seham (*J. Lab. Clin. Med.*, 1923, **8**, 818—824).—A new apparatus is described. The ammonium sulphate globulin test is negative in the majority of ultrafiltrates of normal blood serum. The ultrafiltrates of non-syphilitic and syphilitic blood give a reduction of the colloidal gold solution in almost all cases. The ultrafiltrates of normal cerebrospinal fluid give no colloidal gold curve. The reduction of colloidal gold solution by ultrafiltrates from syphilitic spinal fluids seems to vary with the quantity of the substance reducing the colloidal gold solution present in the original spinal fluid. The substance giving the Wassermann reaction in syphilitic blood does not seem to be ultrafiltrable.

Chemical Abstracts.

Calcium-ion Concentration of Blood Plasma. E. J. Bigwood (*Bull. Soc. Chim. biol.*, 1924, **6**, 118—141).—In 20 normal subjects the calcium-ion concentration varied from 22 to 28 mg. per litre of venous blood plasma. The individual variations in any one subject are closely parallel to the variations in p_{H}, increasing with increasing acidity and *vice versâ*. Such a parallelism does not exist between the calcium-ion and bicarbonate-ion concentrations. J. P.

Effect of Fasting (and Re-feeding) on the Calcium and Inorganic Phosphorus in Blood Serums of Normal and Rachitic Rats. A. W. Cavins (*J. Biol. Chem.*, 1924, **59**, 237—242).—After fasting, the subnormal quantities of inorganic phosphorus present in the serum of rachitic rats increased approximately to normal, and the rickets healed concurrently. In the case of normal rats, there was no similar rise in the inorganic phosphorus in the serum after fasting. W. O. K.

Dynamics of Phosphoric Acid in the Blood. H. Lawaczeck (*Biochem. Z.*, 1924, **145**, 351—371).—The free phosphoric acid of whole blood was found to vary between 7·8 and 18·2 mg.%. When the blood was kept at or below body temperature part of the inorganic was converted into organic phosphate and this conversion was increased by the passage of air or hydrogen through the blood, but it did not occur if the blood had been previously warmed at 44—45°. The reverse conversion of organic into inorganic phosphate resulted from passing carbon dioxide. The reversible interconversion: inorganic $\rightleftarrows$ organic phosphate was found to proceed towards the right in the presence of phosphates, bicarbonate, and calcium, and towards the left in the presence of chlorides, water (hæmolysis), potassium, and sodium, but the cations mentioned were active only in hæmolysed blood. Both inorganic and organic phosphorus compounds passed from the serum into the corpuscles, and *vice versâ*.

The phosphates taking part in the above changes are acid-soluble, but hexosephosphate, which appears to be a product of the synthetic phase of the reaction, is not subject to the reverse hydrolytic change. J. P.

Proteins of Immune Sera, especially the Ratio of Globulin to Albumin (Protein Index). S. Bächer and M. M. Kosian (*Biochem. Z.*, 1924, **145**, 324—343).—An investigation of the amounts of protein precipitable from various normal and immune sera by one-third and one-half saturation with ammonium sulphate. Wide differences exist in the values obtained from the same types of sera from different animals, whilst old sera have a higher protein index than fresh sera and are thus regarded as more labile. Diphtheria sera (horse) show a higher total protein content than the normal, and absolute and relative increases in globulin, notably in pseudoglobulin, and decreases in albumin. During immunisation the lability of horse sera progressively increases, but this is not directly related to the formation of antitoxin. Immunisation of the horse against toxins other than diphtheria does not produce analogous results, nor does diphtheria toxin produce the same effects when injected into oxen. The increased lability of the proteins of old sera is associated with a similar alteration in the ease with which the antitoxin may be salted out with ammonium sulphate. J. P.

Action of Thrombin. IX. Blood Clotting. E. Wöhlisch (*Biochem. Z.*, 1924, **145**, 279—285).—The observation of Stuber and Sano (A., 1923, i, 410) that thrombin prepared by Schmidt's method, when separated from a solution of fibrinogen by a semi-permeable membrane, causes the fibrinogen to clot, was not confirmed when proper controls were employed. The views of these authors (*loc. cit.*) regarding the difference between the thrombin of fresh serum and that precipitated by alcohol according to Schmidt's process are not supported. J. P.

Nature of the Antihæmolytic Property of Heated Sera. G. Milkovitch (*Compt. rend. Soc. Biol.*, 1923, **89**, 877—879; from *Chem. Zentr.*, 1924, i, 356).—Hæmolysis is conditioned, not simply by the presence of a hæmolytic agent, but also by certain chemical factors, in particular the reaction, which must be to a certain degree alkaline. From experiments with human sera heated at

56° it is concluded that the presence of a specific "antihæmolysin" is improbable and that heating simply results in the production of chemical conditions unfavourable to hæmolysis. G. W. R.

Coagglutinating and Precipitating Action of Ricin. G. DI MACCO (*Z. Immunit.*, 1923, **38**, I, 467—488; from *Chem. Zentr.*, 1924, i, 493—494).—In addition to the direct agglutinative effect of ricin on certain blood-corpuscles, agglutination with corpuscles on which it cannot by itself exert any action, can be produced in the presence of serum from other animals. This coagglutination is not shown when ricin is first allowed to react with the serum in the absence of blood-corpuscles. Coagglutination is related to the precipitating action of ricin; it is considered to be physico-chemical in nature. G. W. R.

Precipitin Reactions of a Crystalline Globulin from Human Urine. H. S. EVERETT, S. BAYNE-JONES, and D. W. WILSON.—(See ii, 432.)

Potassium Fluoride as Preservative for Blood. R. H. MAJOR (*J. Amer. Med. Assoc.*, 1923, **81**, 1952).—In the absence of bacteria, clotting is prevented, and the sugar and carbon dioxide tension are unchanged during 7 days when potassium fluoride is added to blood. CHEMICAL ABSTRACTS.

Use of Formaldehyde for the Preservation of Blood Specimens. J. C. BOCK (*J. Biol. Chem.*, 1924, **59**, 73—76; cf. *ibid.*, 1920, **44**, 203).—The use of formaldehyde for preservation of blood for determinations of sugar by the method of Folin and Wu is inadvisable, as five of the six samples of formalin tested gave rise to markedly high results. W. O. K.

Animal Calorimetry. XXIV. Oxidation of Mixtures of Carbohydrates and Fat. A Correction. G. LUSK (*J. Biol. Chem.*, 1924, **59**, 41—42).—Corrections are given of errors in the standard table of Luntze and Schumberg ("Studien zu einer Physiologie des Marsches," Berlin, 1901, 361), showing the caloric value of 1 litre of oxygen used to oxidise mixtures of carbohydrates and fats. W. O. K.

Clinical Calorimetry. XXXV. A Graphical Representation of the Respiratory Quotient and the Percentage of Calories from Protein, Fat, and Carbohydrate. E. F. DU BOIS (*J. Biol. Chem.*, 1924, **59**, 43—49).—Graphs have been constructed from which it is possible to determine rapidly the number of calories produced by each litre of oxygen, knowing the total respiratory quotient and the percentage of calories furnished by protein. W. O. K.

Clinical Calorimetry. XXXVI. A Graphic Method of Determining certain Numerical Factors in Metabolism. A. M. MICHAELIS (*J. Biol. Chem.*, 1924, **59**, 51—58).—A graph is given from which it is possible to determine easily the total calories produced when 1 litre of oxygen is used in the combustion of a mixture of fats, proteins, and carbohydrates, from a knowledge of the urinary nitrogen, the total oxygen consumed, and the total respiratory quotient. From another graph, the percentage of calories derived from protein, fat, and carbohydrate, and that of oxygen used in the oxidation of each, may be read. W. O. K.

Thermochemistry of Protein Behaviour. J. H. MATHEWS and B. W. ROWLAND (*Colloid Symposium Monograph, Univ. Wisconsin,* 1923, 227—243).—Fixed amounts of 0·5*N*-hydrochloric acid were added to gelatin solutions of varying concentrations at 40° and the thermal change was recorded in Browne's adiabatic calorimeter. When in concentration greater than about 2%, gelatin containing 1·3% of ash shows markedly different results from ash-free isoelectric gelatin. Collateral experiments are described with gelatin and glycine. CHEMICAL ABSTRACTS.

Formation in the Injured Liver of a Compound Similar to Dextrose but Unsuitable for the Organism. VARELA and RUBINO (*Arch. exp. Path. Pharm.*, 1924, **101**, 316—334).—The occurrence of hypoglycæmia or of abnormally low hyperglycæmia after the oral administration of 10—20 g. of dextrose or lævulose is taken as an indication of the presence of a sugar unsuitable for utilisation. In certain diseases of the liver, this appears to obtain. It is suggested that the formation of glycogen does not involve merely the polymerisation of dextrose, but that there is a complex assimilation process. W. O. K.

Stimulus of Food on Intermediary Metabolic Processes. I. W. LAUFBERGER and J. A. ŠEFČÍK (*Biochem. Z.*, 1924, **145**, 274—278).—The oral administration of peptone or egg-albumin to rabbits produced a hyperglycæmia within 5 minutes. Mechanical stimulation of the gastric mucous membrane or the administration of olive oil had no influence on the blood-sugar. J. P.

Preparation of Insulin. N. F. FISCHER (*Amer. J. Physiol.*, 1923, **67**, 57—64).—The method of Doisy, Somogyi, and Shaffer (*J. Biol. Chem.*, 1923, **55**, xxi) is modified by effecting the final precipitation in two stages, with 1 and 8 volumes of alcohol, respectively. The first fraction is toxic, and produces a rise in the blood-sugar; the second is active, and of a potency which is the greater the smaller the amount of toxic substance present. Pancreas from old cows yielded only 100 units of insulin per kg., whilst that from calves yielded 1000 units. A. A. E.

Insulin-like Substance in the Kidney, Spleen, and Skeletal Muscle. J. S. ASHBY (*Amer. J. Physiol.*, 1923, **67**, 77—82).—A substance extracted from the kidney, spleen, and muscle of normal dogs and cattle, after the removal of the "toxic fraction," behaved similarly to insulin in producing hypoglycæmia in rabbits. Hypoglycæmia produced by the kidney extract was maintained for the unusually long period of at least 24 hours. A. A. E.

Amount of Available Insulin in the Pancreas of Domestic Animals. F. Fenger and R. S. Wilson (*J. Biol. Chem.*, 1924, **59**, 83—90).—The average yield of insulin from 1 kg. of fresh pancreas of cattle, sheep, or pig was from 1500 to 2200 rabbit units. The methods of purification and standardisation of the insulin are described in detail. W. O. K.

Disposal of Fat in the Organism. F. Köszeg (*Arch. exp. Path. Pharm.*, 1924, **101**, 305—315).—Iodipin (Merck), a fat containing iodine, was introduced in an emulsified form into the jugular vein of a dog. The quantities of iodine, up to about 2% of the weight of tissue, accumulated in the lung, were larger than was found in the liver or spleen. These results lend support to the view that the lung is active in the removal of fat from the blood-stream. W. O. K.

Autolysis. X. The Autolysis of Muscle. K. K. Chen and H. C. Bradley (*J. Biol. Chem.*, 1924, **59**, 151—164).—The rate of autolysis of the muscles of warm-blooded animals, as measured by the production of amino-acids not precipitated by trichloroacetic acid, is at a maximum at p_H 4·5—5·0. This agrees with the fact that *in vivo* atrophy of muscle-tissues follows conditions leading to an acidosis in the muscle-cells. In warm-blooded animals, there appears to be a relation between the activity and pigmentation of the muscle and the degree of autolysis, and similarly in the case of fish-muscle, the degree of autolysis appears to be determined by the activity of the muscles. In the molluscs examined, autolysis is slight and practically unaffected by reaction. W. O. K.

Amino-acids in Nutrition. VI. Nature of the Supplementary Value of Protein-free Milk to the Total Proteins of the Milk. VII. Cause of Nutritive Inadequacy of the Proteins of the Georgia Velvet Bean (*Stilzilobium Deeringianum*). B. Sure (*J. Metabolic Res.*, 1923, **3**, 373—382, 383—391).—VI. The effect is attributed to cystine or some other organic sulphur compound which may be transformed into cystine, and to traces of tyrosine in addition.

VII. The inadequacy is due to indigestibility and to deficiency of amino-acids, the latter being remedied by the addition to the diet of casein and cystine. Chemical Abstracts.

Metabolism of Sulphur. VI. Oxidation of Cystine in the Animal Organism. II. H. B. Lewis, H. Updegraff, and D. A. McGinty (*J. Biol. Chem.*, 1924, **59**, 59—71).—The sulphur in dibenzoylcystine which has been subcutaneously injected into rabbits is not oxidised, but as in the case of phenyluraminocystine (Lewis and McGinty, *ibid.*, 1922, **50**, 303; **53**, 349) it is partly reduced to form the sulphydryl group before excretion in the urine. When dibenzoylcystine is administered orally, a part of the sulphur is oxidised, but this is probably because the compound is partly hydrolysed into benzoic acid and cystine in the alimentary canal. W. O. K.

Substitution of Taurine for Cystine in the Diet of Mice. M. L. Mitchell (*Austral. J. Exp. Biol.*, 1924, **1**, 5—9).—That taurine can replace cystine to a considerable extent is suggested by the fact that the addition of either to a cystine-deficient diet produces growth which does not take place otherwise, and ceases immediately the taurine or the cystine is removed. O. O.

Metabolism of Benzoic Acid in the Human Organism. J. Neuberg (*Biochem. Z.*, 1924, **145**, 249—273).—After the administration of 10 to 15 grams of sodium benzoate to human subjects with normal or impaired kidney functions, no free benzoic acid was found in the urine. The sodium benzoate appears in the urine, not only as hippuric acid (90%), but also as (possibly) benzoylglycuronic acid (10%). It is concluded that methods of determining hippuric acid based on the determination of the benzoic acid freed by hydrolysis give results which are too high. J. P.

Nutrition and Growth on Diets Highly Deficient or Entirely Lacking in Preformed Carbohydrates. T. B. Osborne and L. B. Mendel [with H. C. Cannon] (*J. Biol. Chem.*, 1924, **59**, 13—32).—Rats fed on a diet composed of protein, with varying proportions of fat, inorganic salts, and some source of vitamins, but containing no preformed carbohydrates, showed in many instances good growth, although, as a rule, the male rats did not attain weights greater than about 250 g. W. O. K.

Vitamin Potency of Cod-liver Oil. A. D. Holmes (*J. Metabolic Res.*, 1923, **3**, 393; cf. *ibid.*, 1922, **2**, 113, 361).—The liver oil of emaciated cod caught in March has not so high a vitamin-*A* potency as that from well-nourished fish caught in later seasons. Chemical Abstracts.

Experimental Rickets. XXIV. Effect of certain Extracts of Plant Tissues on Florid Rickets. P. G. Shipley, E. M. Kinney, and E. V. McCollum (*J. Biol. Chem.*, 1924, **59**, 165—175).—Ether, alcohol, and water extract from lucerne leaves a substance which cures rickets in rats. Lucerne, extracted by ether, does not induce healing. Ether extracts an antirachitic vitamin from clover blossom, but, on the other hand, extracts of dry spinach, Brussels sprouts, cabbage, celery, tomato, and sweet potato were without antirachitic effect. W. O. K.

Experimental Rickets. XXV. Antirachitic Effect of certain Oils. P. G. Shipley, E. M. Kinney, and E. V. McCollum (*J. Biol. Chem.*, 1924, **59**, 177—182).—The following oils have no antirachitic effect: oil of sandalwood, oil of lemon, oil of orange-peel, oil of palm, fraction of butter fat insoluble in alcohol, Japan wax, oil of spice, oil of fennel seed, spermaceti, and sperm oil. Oil of cloves and the alcoholic extract of butter fat contain antirachitic vitamin. W. O. K.

Value of Bezssonoff's Reaction for indicating the Presence of Vitamin-*C* in the Juice of Sauerkraut. P. E. Wedgwood and F. L. Ford (*Bull. Soc. Chim. biol.*, 1924, **6**, 217).—A sample of the juice of sauerkraut which gave a blue coloration with Bezssonoff's reagent (*ibid.*, 1923, **4**, 83) failed to protect guinea-pigs from scurvy. It is concluded that Bezssonoff's reagent is not an infallible indicator of vitamin-*C*. C. T. G.

Additional Requirement for the Test with the Reagent for Vitamin-*C*. N. BEZSSONOFF (*Bull. Soc. Chim. biol.*, 1924, **6**, 220). —A reply to Wedgwood and Ford (see preceding abstract). A blue coloration indicates the presence of vitamin-*C* only if the colour is intensified on heating the liquid for a short time. If the colour is reduced or disappears on heating, vitamin-*C* is absent. The maximum dose used by Wedgwood and Ford in their experiments on guinea-pigs is considered to be too small to prove that vitamin-*C* is absent. C. T. G.

Persistence of Vitamin-*C* in the Livers of Rats on a Scorbutic Ration. S. LEPKOVSKY and M. T. NELSON (*J. Biol. Chem.*, 1924, **59**, 91—96).—The livers of rats fed from soon after the time of weaning on a ration as far as possible free from vitamin-*C* contain marked quantities of this vitamin as shown by the effect on the growth of guinea-pigs fed on a diet free from vitamin-*C*. A second generation of rats also fed on a diet free from vitamin-*C* likewise showed no diminution of this vitamin in the liver. W. O. K.

Importance of Zinc on the Nutrition of Animals. Experiments on Mice. BERTRAND and BENZON (*Bull. Soc. Chim. biol.*, 1924, **6**, 203).—It was found impossible to remove all traces of zinc from natural food materials without also removing vitamin-*B*, with which the zinc appeared to be associated. A synthetic food, based on the composition of wheat, was therefore used. Mice receiving the synthetic food with the addition of an amount of zinc as sulphate equivalent to that present in a normal diet of wheat lived 25—50% longer than those receiving the synthetic food alone. In the absence of any supply of zinc in the food, the amount present at the beginning is retained throughout life, whilst, if zinc be given, the original amount present is about doubled. C. T. G.

Non-reciprocal Permeability. III. Non-reciprocal Permeability of Ions and of Colouring Matters. E. WERTHEIMER (*Pflüger's Archiv*, 1923, **200**, 354—365; from *Chem. Zentr.*, 1924, i, 346; cf. *Pflüger's Archiv*, 1923, **200**, 82).—The non-reciprocal permeability shown by the cuticular membrane of frogs is confined to sodium ions. Other cations pass equally freely in both directions. Anions are without influence. Colouring matters behave differently according as they are acidic or basic, the former passing the membrane in an inward direction and the latter in an outward direction. Some acidic and basic colouring matters can pass in either direction. The phenomena are influenced by the reactions on the inner and outer side of the membrane. By making use of non-reciprocal permeability, mixtures of colouring matters may be separated. G. W. R.

Radioactivity of Living Cells. A. NODON (*Compt. rend.*, 1924, **178**, 1101—1102).—The radioactivity of living cells has been demonstrated by photographic means. A sample of barium-radium sulphate, a living insect (*Pœcicoloris*), and a green leaf were confined separately in boxes so as to be able to affect a photographic plate, without coming into contact with the sensitive surface. After 20 hours' exposure, the radium salt gave a strong impression, the insect a more feeble impression, and the leaf a thin film. The activity indicated is of the same order as that indicated by electrometric measurements. [Cf. this vol., i, 347.]

A. B. H.

Coagulation and Structure of the Egg. J. AMAR (*Compt. rend.*, 1924, **178**, 803—805; cf. this vol., ii, 144).—Desiccation of birds' eggs over sulphuric acid showed that egg-white and egg-yolk contain 86% and 48% of water, respectively. Desiccation and re-hydration are completely reversible, unless structural changes (such as are caused by heating or by alcohol) intervene. The dried white contains spiraloid forms (insoluble albumin) in a homogeneous mass (soluble albumin). Sodium chloride does not cause the coagulation of the white or the yolk. The chlorides of potassium, magnesium, calcium, barium, and zinc effect coagulation to an increasing amount (in the order given). Sodium phosphate (present in the egg) hinders coagulation.

E. E. T.

Sugar in the Cerebrospinal Fluid. G. H. MOATES and J. J. KEEGAN (*J. Lab. Clin. Med.*, 1923, **8**, 825—828).—The normal range of cerebrospinal fluid sugar is 0·040—0·068%. The concentration is increased in most cases of epidemic encephalitis but decreased in infectious meningitis. There is no apparent relation between the sugar content of the cerebrospinal fluid and the Wassermann reaction, colloidal gold curve, cell count, globulin, or total protein. CHEMICAL ABSTRACTS.

Bile Secretions. IV. Colorimetric Determination of Bile Acids in Human Body Fluids. F. ROSENTHAL and F. LAUTERBACH.—(See ii, 431.)

Mechanism of Muscular Action. O. W. TIEGS (*Austral. J. Exp. Biol.*, 1924, **1**, 11—29).—It is considered that lactic acid is liberated from only one of the excitable membranes, and at the same time the other membrane must liberate a basic substance, hitherto unrecognised. When this happens, the processes constituting a muscle twitch must occur and their nature can be explained on a physico-chemical basis. O. O.

Alteration of the Constituents of Preserved Flesh. I. A. SMORODINZEV and A. N. ADOWA (*Z. physiol. Chem.*, 1924, **135**, 41—48).—Large quantities of salt solution were pumped into the aorta shortly after killing, and the extractive substances in the muscle-tissues examined after storage for 15 months. The creatinine content was the same as that of fresh flesh, whilst the creatine was reduced to one-fifth or one-tenth. The fact that there was no increase in the amount of methylguanidine suggests that this compound does exist in the tissues and is not necessarily the product of an oxidation occurring during the extraction of creatinine (cf. Ewins, A., 1916, i, 528). E. M. C.

Oxidising Power of the Nuclei of the Epithelium of the Renal Canaliculi of *Perca fluviatilis*. M. Manquat (*Compt. rend.*, 1924, **178**, 972—974).—The nuclei of the epithelial cells of the renal canaliculi of the perch appear to possess oxidising properties, since they become blue when indigo-carmine is injected into the alimentary canal, whereas the cytoplasm remains colourless. This phenomenon was not observed with any of the other species of fresh-water fish examined. T. H. P.

Venom of *Lachesis ammodytoides*. B. A. Houssay and J. Negrete (*Compt. rend. Soc. Biol.*, 1923, **89**, 751—753; from *Chem. Zentr.*, 1924, i, 491).—The venom of this Argentine snake is golden-yellow and contains 34—40% of water. It precipitates the anti-serum for *Lachesis alternatus*, but only slightly that for *Crotalus terrificus*. It has no amylolytic effect and does not attack neutral fats. A description of its physiological effects is given. G. W. R.

Excretion of Creatinine by the Kidneys. V. Cantinieaux (*Compt. rend. Soc. Biol.*, 1923, **89**, 848—851; from *Chem. Zentr.*, 1924, i, 358).—The amount of creatinine eliminated in the urine of healthy men is a function of the total creatinine (preformed creatinine + creatine) in the blood. The relationship is expressed according to Ambard's formula by the constant 0·07 for normal individuals. In cases of depressed renal activity there is a parallelism with the constant for urea. The formulæ of Austin, of Stillman, and of Van Slyke give similar results. No constant results are given when the amount of preformed creatinine in the blood alone is used in the above formulæ. G. W. R.

Electropy. VII. Excretion of Electropic Dyestuffs and Carbinols. L. Karczag and L. Paunz (*Biochem. Z.*, 1924, **145**, 345—350).—Electropic dyestuffs of the triphenylmethane group administered subcutaneously or intravenously to rabbits or guinea-pigs were found in the urine, bile, cerebrospinal fluid, aqueous humour of the eye, peritoneal exudate, and amniotic fluid as colourless carbinols. The less the dispersion of the dyestuff the more slowly is it excreted; the most highly dispersed dyestuffs are excreted by the kidney whilst less highly dispersed dyes are found in the bile. The electrostatic charge on the particles of the dyestuffs is of importance in their conversion and excretion. J. P.

Porphyrin Formation. I. O. Schumm (*Z. physiol. Chem.*, 1924, **133**, 308—320).—The increase in the porphyrin content of the fæces, associated with diet (A., 1923, i, 732), is considered as originating from a constituent of the flesh. The porphyrin prepared from rotting flesh has been examined spectroscopically; it differs from coproporphyrin, but appears to resemble closely the porphyrin prepared from blood by the author, and also that described by Kämmerer and Fischer (cf. Fischer and Schneller, A., 1923, i, 1244). Coproporphyrin could not be found in fresh beef or in frozen meat. O. O.

Correction of "Natural Porphyrins." III. O. Schumm (*Z. physiol. Chem.*, 1924, **133**, 298—307; cf. Fischer and Schneller, A., 1923, i, 1244).—Mainly polemical. The author claims priority in this work, and sees no reason to change the views put forward in his previous paper (A., 1923, i, 631). O. O.

Menstruation and the Choline Balance. E. Sieburg and W. Patzschke (*Z. ges. exp. Med.*, 1923, **36**, 324—343; from *Chem. Zentr.*, 1924, i, 572).—The choline content of the sweat was found to be 80—100 times normal and of the serum 2—15 times normal during menstruation. Intravenous injection of 0·5 g. of choline chloride in women resulted, in half the cases investigated, in a diminished rate of coagulation of the blood. G. W. R.

Relation of the Chemical Constitution of certain Organic Arsenical Compounds to their Action on the Optic Tract. A. G. Young and A. S. Loevenhart (*J. Pharm. Expt. Ther.*, 1924, **23**, 107—126).—Arsenical drugs with quinquevalent arsenic, such as atoxyl, arsacetin, and tryparsamide, frequently affect the optic tract and may produce blindness, whilst certain tervalent arsenic compounds, such as arsphenamine, do not have this effect. Sixteen arsenical compounds of similar constitution were tested by intravenous administration to rabbits, and it was found that the valency of the arsenic was not the most important factor. Optic lesions were produced by compounds containing an amino group or a substituted amino group in the para-position to the arsenic, but were not produced when the amino group was in the ortho- or meta-position. E. M. C.

Effect of Compounds Related to Hydrazine in Producing Anhydræmia and Experimental Anæmia. M. Bodansky (*J. Pharm. Expt. Ther.*, 1924, **23**, 127—132).—The destruction of red corpuscles by subcutaneous injection into dogs of certain hydrazine derivatives has been studied with a view to the experimental production of anæmia. Hydrazine gave a temporary increase in blood concentration (anhydræmia) followed by a slight anæmia. Phenylhydrazine, acetylphenylhydrazine, and *p*-bromophenylhydrazine produce rapid destruction of red corpuscles; methylphenylhydrazine and diphenylhydrazine have similar although less marked effects, whilst *s*-di*iso*propylhydrazine, hydrazobenzene, and 2 : 2′-azobispropane cause a moderate amount of destruction. Mild anæmias were produced in rabbits by azobenzene, azoxybenzene, diazobenzene, and aminoazobenzene; diphenylcarbazide and *p*-hydrazinobenzoic acid have no effect on the blood. Compounds which are especially destructive of liver-tissue were found most effective in producing anhydræmia. E. M. C.

Chemotherapeutic Experiments with Chaulmoogra and Allied Preparations. O. Schöbl (*Philippine J. Sci.*, 1923, **23**, 533—542).—Chaulmoogra oil and its derivatives exert, *in vitro*, a pronounced growth-inhibiting action on *Bacillus tuberculosis*. This inhibition is specific and is noticeable at dilutions of the oil at which no inhibition of non-acid-fast bacilli can be discerned. Oils obtained from plants related to *Taraktogenos Kurzii* have a property similar to that of chaulmoogra oil with regard to *B. tuberculosis*. *Hydnocarpus Wightiana*, *H. alcalœ*, *H. subfalcata*, and *H. venenata*, all containing the optically active acids, show antiseptic power *in vitro*, decreasing in the order mentioned. Oil derived from *Gynocardia odorata*, a plant closely related to *T. Kurzii*, was inactive towards *B. tuberculosis*; it lacks the optically active fatty acids. The growth-inhibiting power of the sodium salts of chaulmoogra oil acids appears to vary, the soap made from the total fatty acids inhibiting the growth of *B. tuberculosis* to a higher degree than does that made from a fraction of the acids. A sodium salt prepared from the isolated hydnocarpic acid approaches closely in strength the soap from the total fatty acids, whilst the sodium salt of chaulmoogric acid is much weaker in its action. H. C. R.

Chemotherapeutic Experiments with Chaulmoogra and Allied Preparations. II. Comparison of the Antiseptic Power of Chaulmoogra Oil with that of other Vegetable and Animal Oils. O. Schöbl (*Philippine J. Sci.*, 1924, **24**, 23—27).—A series of 42 different oils, including vegetable oils, essential oils, and animal oils, was examined according to the technique previously described for their inhibitory effect on the growth of *Bacillus tuberculosis*, *Vibrio choleræ*, and *Staphylococcus* in glycerol meat infusion agar culture. Certain vegetable oils other than those containing optically active fatty acids inhibited the growth of acid-fast bacteria *in vitro*. None of the vegetable oils proper that were investigated inhibited the growth of acid-fast bacteria at such a high dilution as do the chaulmoogra and *Hydnocarpus* oils, which contain optically active fatty acids. Certain essential oils and oils containing volatile constituents, such as cinnamon oil, show a very high selective inhibitory action on acid-fast bacteria. H. C. R.

Toxins. I. Ricin. P. Karrer, A. P. Smirnoff, H. Ehrensperger, J. van Slooten, and M. Keller (*Z. physiol Chem.*, 1924, **135**, 129—166).—The purified products obtained by the fractionation of ricin, tested by intravenous injection into rabbits, showed an extraordinary constancy of toxicity, the lethal dose being 0·005 to 0·003 mg. per kg. live weight. Ricin is not adsorbed by kaolin; basic aluminium sulphate adsorbs the toxic constituents, whilst aluminium hydroxide adsorbs the less toxic constituents. Fractional precipitation with salts of heavy metals affects ricin preparations adversely. The destruction by trypsin of ricin, as measured by the toxicity of the digestion mixture and of the undigested residue at different stages, ran parallel to the protein hydrolysis, so that the toxic action of ricin appears to be a function of the protein. It has not been possible to concentrate the toxic principle beyond a certain point, and yet such preparations are not single substances, since less toxic materials may be removed by adsorption and different preparations give different equivalents on titration in alcohol. A complete analysis by the Fischer and Dakin methods has been made of the amino-acids after hydrolysis of the protein. The original must be consulted for details.

E. M. C.

Comparison of the Activities of Antiseptics on Bacteria and on Leucocytes. A. Fleming (*Proc. Roy. Soc.*, 1924, **B, 96,** 171—180).—Leucocytes have a rapid lethal action on bacteria, distinct from their phagocytic action. There is, for all common antiseptics, with the possible exception of flavine, a range of concentrations (below that at which bacteria are killed) within which the bactericidal power of leucocytes is destroyed ("antibactericidal zone"). Thus the presence in blood of an antiseptic in a concentration within this zone, so far from preventing the growth of bacteria, may actually favour it. W. O. K.

Mechanism of the Action of Bismuth Derivatives in Trypanosomiases and Spirilloses. C. Levaditi and S. Nicolau (*Ann. Inst. Pasteur*, 1924, **38,** 179—239).—A detailed account of work already published in brief (*Compt. rend.*, 1923, **176,** 1189). W. O. K.

Degradation of Starch by Animal Amylases. O. Holmbergh (*Ark. Kemi, Min., Geol.*, 1923, **8,** No. 33, 1—5).—The author has investigated the action on 2% starch solution of glycerol extracts of dry, powdered liver, prepared by treating the minced liver with ether and acetone. As these preparations contain maltase as well as amylase, parallel experiments were made in all cases with substrates containing only maltose. The velocity of the amylolytic reaction is diminished to the extent of about 32 (75)% by the presence of 0·4 (3)% of maltose. Liver-amylase is far more sensitive to the influence of maltase than is malt-amylase. When the maltose formed is removed by either dialysis or fermentation, the hydrolysis of the starch is quantitative. In all the experiments the reaction of the medium was adjusted to p_H 6·9, which is the optimum acidity for amylolytic changes.

Dialysis of 1% starch solution proceeds far more rapidly when the starch is prepared by Zulkowski's method (A., 1880, 865) than when Lintner's soluble starch is used. T. H. P.

Action of Potassium Iodide on the Saccharification of Starch by Various Amylases. O. Holmbergh (*Biochem. Z.*, 1924, **145,** 244—248).—Potassium iodide inhibits the formation of maltose from starch by the action of malt-amylase, the action in this respect resembling that on liver-amylase (cf. Holmbergh, *Z. physiol. Chem.*, 1924, **134,** 68). It increases the similar actions of salivary and pancreatic amylases. The two latter amylases therefore differ from liver-amylase. The varying extents to which dextrins and maltose are formed by the action of liver-amylase on starch have been investigated in concentrations of potassium iodide varying from 0·1*N* to 2·0*N*. The amount of maltose formed when the achromic point is reached diminishes with increasing concentrations of the iodide, but the rate of formation of the dextrins themselves is increased. J. P.

Hydrolysis of Starch by Emulsin. R. KUHN (*Z. physiol. Chem.*, 1924, **135**, 12—15).—Preparations of emulsin from both bitter and sweet almonds brought about a considerable hydrolysis of soluble potato starch, at an optimum acidity of p_H 5·5. A specially purified sample of the enzyme converted the amylase of the starch grains quantitatively into maltose. E. M. C.

Digestion of Gums by Organisms and Enzymes. Digestion of Cherry Tree Gum *in vitro*. A. VOSKRESSENSKY (*Bull. Soc. Chim. biol.*, 1924, **6**, 226).—Experiments are recorded on the breaking down of cherry tree gum, as indicated by the production of reducing sugars, by the enzymes of various plants, micro-fungi, yeasts, and bacteria, and by enzymes contained in various animal organs. Several enzymes, of which some occur in the digestive tract of animals, can decompose the gum to some extent, but the amount of hydrolysis is much less than can be obtained with mineral acids.

Rats can live on a ration consisting largely of cherry tree gum but not on the gum alone. Various insects and molluscs refused to eat gum. C. T. G.

Invertase. V. R. WILLSTÄTTER and K. SCHNEIDER (*Z. physiol. Chem.*, 1924, **133**, 193—228).—In continuation of previous work (A., 1923, i, 69), it has been found that direct adsorption of invertase from yeast autolysates by kaolin can be brought about without preliminary adsorption by alumina, and without the considerable dilution formerly used, if the acidity of the solution is increased to the maximum limit (*e.g.* 10% acetic acid) consistent with the non-destruction of the enzyme.

Using the above improved method, several invertase preparations have been separated into easily and difficultly adsorbed fractions, and the former have been further subdivided by fractional elution. An examination of the various fractions so obtained, furnished evidence that the nitrogen content and the activity of the enzyme preparations were not proportional. Indeed, in certain cases active preparations which failed to give any protein reactions were obtained. Since in earlier work other preparations have been obtained which were free from carbohydrates, it is proved that invertase belongs neither to the proteins nor to the carbohydrates.

After a single adsorption by this method, a preparation of high activity was obtained. When the kaolin treatment was followed by adsorption by alumina, the activity was still further increased. The stability of the enzyme during adsorption varies considerably with the acidity.

The age of the autolysate and its previous purification both have a profound effect on the adsorptive value of kaolin. Whereas with fresh autolysates preliminary precipitation with alcohol is essential for successful adsorption, this is not the case for old autolysates. O. O.

Invertase as an Amphoteric Electrolyte and as a Colloid. H. von Euler and K. Josephson (*Z. physiol. Chem.*, 1924, **133**, 279—297).—Using an invertase preparation of high purity ($If = 240—242$) the authors have obtained, by electrometric determination, values of $4\cdot3 \times 10^{-11}$ and $5\cdot5 \times 10^{-11}$ for K_b, and values of $0\cdot9 \times 10^{-11}$, $0\cdot32 \times 10^{-7}$, and $0\cdot62 \times 10^{-8}$ for K_a. From the values for K_b it is calculated that the molecular weight of invertase cannot exceed 3900. Viscosity measurements showed the isoelectric point to lie between $p_H = 4\cdot5$ and 5; this is also the p_H for maximum adsorption of the enzyme by aluminium hydroxide. The results are discussed in the light of L. Michaelis' theory concerning enzyme action, and the conclusion is drawn that the theory is inadequate. O. O.

Invertase. E. Canals (*Bull. Soc. chim.*, 1924, [iv], **35**, 213—217).—Hydrochloric and phosphoric acids increase the hydrolysing power of dialysed yeast invertase preparations to a slightly greater extent than when undialysed preparations are used, but with sulphuric acid the reverse is the case. E. E. T.

Influence of Stereoisomeric Sugars, Non-hydrolysable Carbohydrates, and Glucosides on the Efficiency of Yeast Invertase. Specificity of Enzymes. VI. R. Kuhn (*Z. physiol. Chem.*, 1924, **135**, 1—11).—The α- and β-forms of *d*-mannose and *l*-arabinose resemble those of *d*-fructose in slowing down the action of invertase on sucrose to the same extent. β-*d*-Galactose resembles β-*d*-glucose in being more active than the α-form, although both forms of *d*-galactose are much more active than the other hexoses studied. The stereoisomeric forms of lactose, maltose, cellobiose, melibiose, gentiobiose, and trehalose are without perceptible effect. The inactivity of inulin suggests that there is no combination of inulin with the invertase. Salicin, helicin, and β-methylglucoside reduce the rate of inversion, but amygdalin is without effect. The α-methylglucoside is many times as active as β-methylglucoside. These results are in agreement with the view that the activity of invertase is determined by its power of combination. E. M. C.

Fermentation Co-enzyme (Co-zymase) of Yeast. II. H. von Euler and K. Myrbäck (*Z. physiol. Chem.*, 1924, **133**, 260—278).—Using small quantities of material, fermentation has been followed in the presence of co-zymase with the following results: the fall in the rate of fermentation can be overcome by the addition of fructose diphosphate; an extract of germinating malt has no influence on the rate; glycerol has no effect, whilst toluene and alcohol exert a retardation; lævulose and dextrose are identical in their action. Zymophosphate causes fermentation to start immediately, and it is suggested that yeast always contains sufficient of this substance to initiate the fermentation. In addition to blood, milk at p_H 5 increases the activity of the co-zymase. The co-zymase present in muscle is probably identical with that present in yeast, but it does not appear to bear any relation to the antineuritic or growth-promoting vitamins. O. O.

Latent Fermenting Powers of Bacteria. I—III. E. C. Grey (*Proc. Roy. Soc.*, 1924, **B**, **96**, 156—170).—The general course of the decomposition occurring during fermentation by *Bacillus coli* in the presence of formates is the same whether the substrate is dextrose or glycerol. In each case, about 25% and 40% of the substrate is converted into carbon dioxide and acetic acid, respectively, but the remaining 35% is mainly lactic acid when dextrose is used, and mainly ethyl alcohol when glycerol is used. In presence of formates, glycol and malonic acid are fermented by *B. coli* with the production of acetic and lactic acids, whilst citric, malic, and tartaric acids yield carbon dioxide, acetic acid, and succinic acid. The yield of succinic acid from dextrose is decreased by the presence of formates, and this is apparently due to the ability of the bacteria to ferment succinic acid under these conditions. On the basis of these and earlier results, the author outlines a simple theory of fermentation, for details of which the original must be consulted. W. O. K.

Enzymic Transformation of Aldehydes. I. Acceleration of the Cannizzaro Reaction by Yeast. K. Josephson and H. von Euler (*Z. physiol. Chem.*, 1924, **135**, 49—60).—The authors emphasise the importance of acidity in controlling the yields of the different products of fermentation. Acetaldehyde is stable in solutions more acid than p_H 8·5. In the presence of living yeast, removal of acetaldehyde occurs even in solutions as acid as p_H 3—4. The reaction velocity is difficult to measure owing to the changes produced by the acetic acid formed, but in the early stages the acetaldehyde decomposition is only slightly less at p_H 4 than at p_H 7. A slight removal of acetaldehyde is caused by boiled yeast suspensions and is probably due to a combination with the proteins of the yeast. *iso*Valeraldehyde gives similar results to acetaldehyde, although the reaction is considerably slower. E. M. C.

Metabolism of Pyruvic Acid in Bacteria. E. Aubel (*Bull. Soc. Chim. biol.*, 1924, **6**, 288).—A continuation of work previously published (Cambier and Aubel, *Compt. rend.*, 1922, **175**, 71). Sodium pyruvate serves as a source of carbon for bacteria. It gives rise in cultures to carbon dioxide, hydrogen, methane, lactic, glycollic, acetic, and formic acids. The energy relationships of the reactions taking place in the formation of these substances from pyruvic acid are discussed.

Working with a bacterium isolated from the Paris water supply, it was found that considerable quantities of dextrose were converted into pyruvic acid, which was then utilised; later, lactic acid made its appearance, but whether this was formed from pyruvic acid or was the product of a separate fermentation of dextrose is uncertain. C. T. G.

Mechanism of the Production of β-Hydroxybutyric Acid by Biochemical Means. LEMOIGNE (*Compt. rend.*, 1924, **178**, 1093—1095).—Continuing previous work (A., 1923, i, 881; this vol., i, 353), the author finds that a new insoluble, crystallisable product may be obtained from macerations of bacteria of the *Bacillus subtilis* group, by means of boiling alcohol. The structure of the pure *substance*, m. p. 118—119°, has not been determined, but alkaline hydrolysis gave 1 mol. of α-crotonic acid, m. p. 72°, and 2 mols. of β-hydroxybutyric acid. The proportion of the two acids was calculated from the observed optical rotation of the alkaline mixture. A. B. H.

Yeast. V. Is Bios a Single Substance? E. J. FULMER and V. E. NELSON (*Proc. Iowa Acad. Sci.*, 1922, **29**, 371; cf. A., 1921, i, 386; *J. Biol. Chem.*, 1922, **51**, 77).—Combination of the absolute alcohol extracts of lucerne with the water extract of the residue produced greater yeast growth than either extract alone. Bios is composed of at least two yeast-growth promoting materials. CHEMICAL ABSTRACTS.

Multiple Nature of Bios. E. J. FULMER, W. W. DUECKER, and V. E. NELSON (*J. Amer. Chem. Soc.*, 1924, **46**, 723—726).—An aqueous extract of lucerne was fractionally precipitated with alcohol and the four resulting fractions were tested for "bios" in a medium containing ammonium chloride, dipotassium phosphate, calcium chloride and carbonate, and sucrose, which was inoculated with yeast. The results obtained showed that bios contains at least two different growth stimulants. C. J. S.

Pancreatic Enzymes. VI. Effect of Lipase on Different Substrates. R. WILLSTÄTTER and F. MEMMEN (*Z. physiol. Chem.*, 1924, **133**, 229—246).—The hydrolysis of methyl butyrate by lipase is accelerated by calcium oleate, but much more so by a mixture of albumin, sodium oleate, and calcium chloride at p_H 8·9. The addition of a large amount of glycerol (33%) still further accelerates the hydrolysis. Both the rate and degree of hydrolysis are directly proportional to the amount of the enzyme present.

In the hydrolysis of triacetin by lipase, the enzyme is activated by salts of bile acids and oleic acid. As in the case of tributyrin (A., 1923, ii, 704), the increase in hydrolysis due to calcium oleate is not further emphasised by the addition of albumin. In the course of the hydrolysis, the effect due to the enzyme diminishes, and this change is due to deterioration of the enzyme.

From a study of the rate of hydrolysis of various esters by various lipase preparations it is concluded that pancreatic lipase is not a mixture of enzymes, but one single enzyme which, however, shows a quantitative specificity as regards its rate of action on different substrates. O. O.

Pancreatic Enzymes. VII. Comparison of Gastric Lipase with Pancreatic Lipase. R. WILLSTÄTTER and F. MEMMEN (*Z. physiol. Chem.*, 1924, **133**, 247—259).—Gastric lipase and pancreatic lipase, from the pig, differ in their behaviour towards activators such as sodium oleate and bile salts, and towards the hydrogen-ion concentration. Further, different preparations of the one enzyme from the same source show inconsistent behaviour. These divergences can, however, be traced to contamination. When gastric lipase is purified by adsorption with kaolin and elution with ammoniacal phosphate solution containing glycerol, these differences disappear, and it is concluded that there is no difference between gastric lipase and pancreatic lipase. Lipase is not present in the organs as a zymogen. O. O.

Enzyme Action. XXV. Comparative Lipase and Protease Actions of the Flexner–Jobling Rat Carcinoma and of different Rat Tissues. XXVI. Comparative Lipase and Protease Actions of different Beef Tissues. XXVII. Comparative Enzyme Actions of Tissue Mixtures and of Tumour-tissue Mixtures in Relation to the Comparative Enzyme Actions of Tumour Extracts Alone. K. G. Falk, H. M. Noyes, and K. Sugiura (*J. Biol. Chem.*, 1924, **59**, 183—212, 213—223, 225—235).—The activities of extracts of various tissues in hydrolysing phenyl acetate, glyceryl acetate, methyl butyrate, benzyl acetate, ethyl acetate, ethyl butyrate, methyl benzoate, ethyl benzoate, *iso*butyl acetate, and protein, were measured. By expressing the results graphically, characteristic differences between the action of the extracts from different tissues are brought out. For details, the original must be consulted. W. O. K.

Protein Studies. III. Decomposition of Silk Fibroin by Fermentation. F. Wessely (*Z. physiol. Chem.*, 1924, **135**, 117—121).—Silk fibroin was dispersed by dissolving it rapidly in cold concentrated hydrochloric acid and neutralising with sodium hydroxide, with rapid cooling. The resulting solution was stable if it contained less than 1·5% of fibroin, but was flocculated by shaking or stirring. The fibroin could be reprecipitated quantitatively by alcohol and ether. On digestion with trypsin, about one-quarter of the fibroin separated as a jelly in 24 hours; the remaining liquid gave no precipitate with 50% alcohol, and contained little nitrogen as amino-acids or as compounds not precipitated by phosphotungstic acid. Similar evidence of decomposition by pepsin was obtained. E. M. C.

Can Copper Salts Act Simultaneously as Oxydases and Peroxydases? R. Dubois (*Compt. rend. Soc. Biol.*, 1923, **89**, 10—11; from *Chem. Zentr.*, 1924, i, 458).—Fehling's solution can act on luciferin, producing luminescence in the same manner as luciferase. The observations of Valdiguié (*Compt. rend. Soc. Biol.*, 1923, **88**, 1091) are confirmed. G. W. R.

Effect on Phenols and their Derivatives of Oxydases of Melanotic Tumours in Chorioidea. J. Mawas (*Compt. rend. Soc. Biol.*, 1923, **88**, 263—265, 332—333; from *Chem. Zentr.*, 1924, i, 354).—The peroxydase from melanotic tumours in chorioidea has no effect on phenol, thymol, phloroglucinol, and naphthol.

With pyrocatechol a colour change with the formation of a precipitate is observed. Pyrogallol and hydroxyquinol are oxidised. A direct relationship appears to exist between the constitution of organic compounds and their ability to be oxidised by enzymes. For example, phenols are only attacked when the hydroxy groups are in the ortho position. The formation of a black pigment is not attributed to a tyrosinase or to the oxidation of tyrosine by a peroxydase. G. W. R.

Action of Laccase. Influence of Concentration of Guaiacol and Pressure of Oxygen. P. FLEURY (*Compt. rend.*, 1924, **178**, 1027—1030).—For concentrations of guaiacol below a certain value, the reaction velocity of laccase was proportional to the concentration of guaiacol, but at concentrations above that value it tended to become constant. Diminution of laccase concentration displaced this zone of inflection in the direction of lower guaiacol concentration. Variation of the oxygen content of the air current affected the reaction velocity only when it was decreased; a similar zone of inflection was observed, which was displaced in the direction of low oxygen concentration as the amount of laccase present decreased. The rate of diffusion of the oxygen into the solution also conditioned the activity of the laccase. H. J. E.

Liver Catalase. S. HENNICHS (*Biochem. Z.*, 1924, **145**, 286—305).—Denoting the "activity" of the catalase present by: (reaction constant) ÷ (dried residue in 1000 c.c. of the reaction mixture), it is shown that liver catalase preparations may be obtained with an "activity" of 532 by adsorption with kaolin and elution with a phosphate mixture of p_H 7·6, by which means a quantitative recovery of the enzyme is achieved. Aluminium hydroxide is also used as an adsorbent (p_H 5—7) and the elution carried out at p_H 8. Two such treatments gave a preparation with an "activity" of 521. Previous preparations of liver and blood catalase by Madinaveitia (*Diss.*, Zurich, 1912) had "activities" of 66·8 and 34·9 respectively, and it is concluded that a considerable advance has been made in purifying the enzyme. The affinity constant of the system catalase–substrate is given as K_M 22. The thermostability of catalase varies with the concentration, dilute solutions being much less stable at 60° than more concentrated solutions. J. P.

Relations between the Physico-chemical State and the Functioning of Protoplasm. Photosynthesis and Respiration. C. FROMAGEOT (*Bull. Soc. Chim. biol.*, 1924, **6**, 169—180).—Pieces of the alga *Ulva lactuca* kept in sea-water containing varying amounts of glycerol showed an output of oxygen which diminished as the concentration of glycerol was increased, and ceased when the latter reached 15%. This effect was reversible when the alga was removed from the glycerol solution provided its concentration had not exceeded 10%. The alga kept in the dark under the same conditions showed an increased absorption of oxygen up to glycerol concentrations of 5%, above which the respiration diminished but did not cease even in concentrations of 40%. Saline solutions of the composition of sea-water and of the same p_H, but with varying concentrations, affected the photosynthetical activity markedly, the latter being at an optimum when the osmotic pressure of the solution was that of sea-water. A similar effect on respiration was not observed, but in very concentrated sea-water it was slightly diminished. It is concluded that physico-chemical alterations of the protoplasm do not affect photosynthesis and respiration in the same way, and that the former process is much more susceptible to such disturbances than is the latter. J. P.

Feeding of Plants with Aldehydes. IV. T. SABALITSCHKA. **Behaviour and Detection of Formaldehyde in Plants and Plant Substances.** T. SABALITSCHKA and H. RIESENBERG (*Biochem. Z.*, 1924, **145**, 373—378).—Fresh leaves of cress plants grown in an atmosphere containing formaldehyde (cf. this vol., i, 475) contained less than 0·5 mg. of formaldehyde per gram, whilst the same amount of leaves after drying contained 0·2 mg., and after extraction with water and alcohol 0·1 mg. The dry residue obtained from the aqueous extract of the leaves contained no formaldehyde. Formaldehyde added to fresh rhubarb or cress leaves made into a pulp with water was fixed wholly or in part. Its presence in fresh cress leaves or in the aqueous distillate from an extract of the leaves could not be demonstrated. J. P.

Water Cultures containing Benzoic Acid. Assimilation of Benzoic Acid by Culture Plants. T. BOKORNY (*Biochem. Z.*, 1924, **145**, 306—308).—Barley seedlings grown in a medium containing benzoic acid (0·016%) appeared to absorb the latter and to give increased growth. The presence of the acid in the plants could not be demonstrated, and it is concluded that it is assimilated and serves as a source of carbon. J. P.

Nitrogenous Substances in Ripening Rye Ears. A. KIESEL (*Z. physiol. Chem.*, 1924, **135**, 61—83).—The total nitrogen content of whole rye ears increased as ripening proceeded; the increase was chiefly in the protein nitrogen, with slight increases in the base and peptone nitrogen and in the amide nitrogen. The ammonia nitrogen remained constant, whilst the amino-acid nitrogen showed a pronounced minimum in one case. Asparagine was absent in each stage. The purine bases decreased markedly as the ripening proceeded. Xanthine, guanine, adenine, and hypoxanthine were separated from one sample. Histidine could be detected only in traces. Arginine was absent, but the arginine fraction contained guanidine, a base, probably agmatine, and an unidentified base. The lysine fraction from the above sample gave tetramethylenediamine, choline, aspartic acid, and phenylalanine. None of these was identified from the second fraction and only choline from the third. This is the first definite record of the isolation of aspartic acid from plants; the possibilities of its being derived from protein hydrolysis are discussed. E. M. C.

Colloidal Properties of Winter Wheat Plants in Relationship to Frost Resistance. R. Newton (*J. Agric. Sci.*, 1924, **14**, 178—191).—The hardiness of wheat plants was found to be related to the imbibition pressure of the leaves in the winter-hardened condition, but not in unhardened leaves. The quantity of hydrophilic colloids contained in the press juice of hardened leaves was directly proportional to hardiness. A. G. P.

Photoperiodism in Relation to Hydrogen-ion Concentration of the Cell Sap and the Carbohydrate Content of the Plant. W. W. Garner, C. W. Bacon, and H. A. Allard (*J. Agric. Res.*, 1924, **27**, 119—156).—The variations which occur in the habit of plants exposed to different day lengths (*ibid.*, 1920, **18**, 553) extend to the acidity of the sap, the carbohydrate content, and the water content of the tissues. Short day plants exposed to long day illumination show a progressive increase in acidity, particularly at the growing point, until the upper parts are more acid than the lower parts. Exposure to short day illumination results in a transitory period of decreased acidity followed by a moderate increase which persists until flowering is initiated. In this case, the acidity in the upper parts is not as high as that found in the lower parts of the plant. The low acidity of the embryonic flower-bud increases to a maximum in the unfolded blossom, in contrast to the developing seed in which there is a decrease in acidity during active growth. Long day plants exposed to short day periods show a low level of acidity, which increases when the day length is increased. *Helianthus annuus*, which is intermediate between the long day and the short day groups, shows changes in acidity which may be typical of either group. Transfer of Cosmos plants from a long to a short day caused a marked increase in reducing sugar in the upper portion of the stem within 48 hours of the transfer. After 2 days the increased sugar was present as polysaccharide, but 12 days later, after the flower-buds appeared, the sugar was present as monosaccharide. At the same time, a considerable increase in the water content of the tissues had occurred. O. O.

Changes in Hydrogen-ion Concentration Produced by Growing Seedlings in Acid Solutions. J. Davidson and E. T. Wherry (*J. Agric. Res.*, 1924, **27**, 207—217).—Wheat seedlings, after growing for several days in tap-water or dilute nutrient solutions, were transferred to dilute solutions of nitric, phosphoric, sulphuric, or hydrochloric acid, and the changes in p_H values observed. The greatest reduction in acidity was with nitric acid for young seedlings and with phosphoric acid for older seedlings. The importance of these acids in plant nutrition suggests that the initial changes of reaction in culture media are due to absorption rather than to neutralisation of the acids by root excreta. The reduction of acidity was less for seedlings grown in nutrient solutions lacking the corresponding anion, owing, apparently, to functional disturbances. Large reductions of acidity in solutions of organic acids were ascribed to the action of micro-organisms. E. M. C.

Insecticides. I. Isolation and Constitution of the Active Constituent of Dalmatian Insect Powder. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 177—201).—The insect powder obtained from the flowers of *Chrysanthemum cinerariifolium* Bocc., was investigated by Fujitani (A., 1909, ii, 825), who obtained from it a highly insecticidal, viscous oil which he termed pyrethrone. By alkaline hydrolysis of this he obtained an alcohol, pyrethrol, and an acid, both of which were inactive. Fujitani's viscous oil is found to contain about 50% of inactive substances, from which the pyrethrol is derived. There are two active constituents present in the oil, termed *pyrethrine* I and II, esters of a ketonic alcohol, *pyrethrolone*, combined with *chrysanthemumcarboxylic acid* and *chrysanthemumdicarboxylic acid*, respectively. The crude oil, the yield of which is 0·5% of the weight of the powder, forms a crystalline mixed semicarbazone, from which the *semicarbazone* of pyrethrine I can be obtained almost pure, m. p. 122—123°. By hydrolysis of the mixed semicarbazones, with methyl-alcoholic sodium hydroxide, the *semicarbazone* of pyrethrolone is obtained, m. p. 200° (decomp.), and by acid hydrolysis of this, the alcohol itself, *pyrethrolone*, a colourless, optically active liquid, b. p. 110—112°/0·1 mm. The acid of pyrethrine I, *chrysanthemumcarboxylic acid*, is an optically active liquid, b. p. 135°/12 mm., and that of pyrethrine II, *chrysanthemumdicarboxylic acid*, is a more viscous, optically active liquid, b. p. 120°/0·1 mm. Neither the alcohol nor the acids have insecticidal properties. The insect powder contains the two active substances, I and II, in the proportions of about 2 : 3; the former is the more active, killing moths at a dilution of 1 in 10,000 in 10 to 20 minutes, whilst the latter takes twice as long (cf. this vol., i, 510, 521, 522, 523). E. H. R.

Phlobaphens. M. DITTMAR (*J. Amer. Pharm. Assoc.*, 1923, **12**, 680—688).—Phlobaphens can be salted out from solution, but if the salt be removed by osmosis the phlobaphen again enters into solution. The dark red solution of a phlobaphen in ethyl alcohol may be reduced by boiling with zinc dust, but the product gradually becomes coloured by atmospheric oxidation. The phlobaphens, which vary considerably in composition, yield oxalic acid when boiled with nitric acid, but when boiled with dilute sulphuric acid do not yield dextrose, although some colour changes result. CHEMICAL ABSTRACTS.

Essence of the Carnation. M. L. S. GLICHITCH (*Bull. Soc. chim.*, 1924, [iv], **35**, 205—207).—The essence extracted from the flowers (0·003% yield) by distillation in steam was a pale green solid of greasy taste and touch with an intense odour resembling that of certain aliphatic aldehydes; m. p. 35—37°; d_{40}^{40} 0·869; $[\alpha]_D$ −8·28° (c=3·148 in benzene). From it a branched chain heptacosane, m. p. 53—55°, was isolated in 31% yield. Other paraffins were also present. Inconclusive evidence of an acetylated compound and of a substance of aldehydic or ketonic nature was obtained. E. E. T.

Organic Chemistry.

Pyrogenic Decomposition of Acyclic Hydrocarbons. H. Gault, F. A. Hessel, and Y. Altchidjian (*Compt. rend.*, 1924, **178**, 1562—1565).—An introductory paper to the systematic study of the pyrogenic decomposition of acyclic hydrocarbons containing at least 16 carbon atoms, with special reference to the effects of temperature, rate of flow of liquid, and period of heating. The apparatus and procedure to be used are described. The preparation of hexadecene by the distillation of cetyl palmitate and of hexadecane by catalytic hydrogenation of hexadecene (cf. Brochet, A., 1914, i, 1069) is described. J. W. B.

Preparation of Acetylenic Hydrocarbons, their Sodium Derivatives, and the Corresponding Acetylenic Acids. L. Meunier and E. Desparmet (*Bull. Soc. chim.*, 1924, [iv], **35**, 481—484; cf. A., 1907, i, 186).—Chloro derivatives of aliphatic aldehydes and ketones react with sodamide, giving the sodium derivatives of the corresponding acetylenic hydrocarbons. Acetylenic hydrocarbons react quantitatively with sodamide to give the corresponding sodium derivatives. Allyl and disubstituted acetylenic hydrocarbons react quantitatively on heating with sodamide, giving the sodium derivatives of the corresponding acetylenes. Ether and similar solvents play no useful part in the absorption of carbon dioxide by the sodium derivatives to form acids.

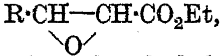
A. B. H.

Partial Dehydration of Aldehydes and Ketones forming Acetylenic Hydrocarbons. Bourguel (*Compt. rend.*, 1924, **178**, 1557—1560).—The dehydrating and chlorinating action of phosphorus pentachloride on methyl *n*-propyl ketone, diethyl ketone, dipropyl ketone, heptaldehyde, acetophenone, and ethyl phenyl ketone, resulting in the formation of acetylenic and ethylenic compounds, is described. Methyl *n*-propyl ketone (1 mol.) treated in the cold with phosphorus pentachloride (1 mol.) forms Δ^{β}-pentinene, $CEt\vdots CMe$ (0·005 mol.), together with the compounds $CHEt{:}CClMe$ (0·35 mol.), and $CHEtCl\cdot CHCl\cdot CH_3$ (0·06 mol.), the latter being detected by conversion into Δ^{β}-pentene by the action of zinc powder and alcohol; much hydrogen chloride is also evolved. It is assumed that it is the enolic form of the ketone which reacts with the phosphorus pentachloride. Diethyl ketone and dipropyl ketone yield the corresponding compounds, whilst heptaldehyde yields Δ^{α}-heptinene, $C_5H_{11}\cdot C\vdots CH$, and chlorinated compounds. Neither acetophenone nor ethyl phenyl ketone gives acetylenic hydrocarbons. J. W. B.

Preparation of Two True Diacetylenic Hydrocarbons. Lespieau (*Compt. rend.*, 1924, **178**, 1565—1567).—On addition of αβ-dibromopropylene in ether to the product of the interaction of pentamethylene dibromide and magnesium shavings suspended in ether, a brisk reaction occurs and from the product, on repeated fractionation, the following compounds have been isolated: (1) Unchanged dibromopropylene; (2) Δ^{a}-*bromo-octene*, $Me\cdot[CH_2]_5\cdot CBr{:}CH_2$, b. p. 60—61°/11 mm., d^{20} 1·158, n_D 1·4715; (3) unchanged pentamethylene dibromide; (4) the alcohol, $CH_2{:}CBr\cdot[CH_2]_5\cdot CH_2\cdot OH$, b. p. 120—121°/11 mm., d^{21} 1·272, n_D 1·499 (*phenylurethane*, m. p. 52·5—53·5°); (5) βκ-dibromo-$\Delta^{\alpha\kappa}$-undecadiene, $CH_2{:}CBr\cdot[CH_2]_7\cdot CBr{:}CH_2$, b. p. 150—151°/10 mm., d^{25} 1·359, n_D 1·504; (6) βο-dibromo-$\Delta^{\alpha o}$-hexadecadiene, $CH_2{:}CBr\cdot[CH_2]_{12}\cdot CBr{:}CH_2$, b. p. 200—202°/10 mm., m. p. −5°, d^{20} 1·221, n_D 1·497. By the action of sodamide on (2) the octinene is obtained in more than 70% yield. By the action of alcoholic potash at the temperature of a water-bath on (5) $\Delta^{\alpha\kappa}$-*undecadi-inene*, $CH{\vdots}C\cdot[CH_2]_7\cdot C{\vdots}CH$, a liquid with an orange-like odour, b. p. 82·5—83°/12 mm., m. p. −17°, d^{21} 0·8182, n_D 1·453, is obtained which yields a yellow precipitate with ammoniacal cuprous chloride and a white *precipitate*, $C_{11}H_{14}Ag_2,2AgNO_3$, with alcoholic silver nitrate. Similar treatment of (6) yields $\Delta^{\alpha o}$-*hexadecadi-inene*, $CH{\vdots}C\cdot[CH_2]_{12}\cdot C{\vdots}CH$, brilliant laminæ, m. p. 44—45°, b. p. 152—155°/12 mm., giving corresponding *copper* and *silver* compounds. J. W. B.

Action of Inorganic Iodides on αβ-Dibromo Compounds. I. Mechanism of the Reaction. C. F. van Duin (*Rec. trav. chim.*, 1924, **43**, 341—358).—The velocity of the reaction between metallic iodides and αβ-dibromo compounds, $R\cdot CHBr\cdot CHBr\cdot R' + 2M'I = R\cdot CH{:}CHR' + I_2 + 2M'Br$, has been measured at 25° in the dark in an atmosphere of carbon dioxide, using potassium iodide as the metallic iodide with αβ-dibromopropionic acid and αβ-dibromo-β-*p*-sulphophenylpropionic acid, respectively. The reaction appears to be termolecular, and it is probable that αβ-di-iodo compounds occur as intermediate products which break down into ethylenic compounds and free iodine, with a velocity great compared with that of the substitution. Cations, except hydrogen ions, exert a strongly positive catalytic influence, and iodine ions act more rapidly than undissociated iodides. Light accelerates the reaction whilst iodine retards it. Calcium salts are slightly more active catalytically than potassium salts. E. H. R.

Spontaneous Combustion during Work with Dichloroethylene. H. Theron (*Chem.-Ztg.*, 1924, **48**, 142).—Spontaneous combustion due to chloroacetylene was observed during the distillation of a large quantity of alcohol containing about 0·25% of dichloroethylene, with sodium hydroxide. A. R. P.

Preparation of Alcohols of the Formulæ $R·CH_2·CH_2·CH_2·OH$ and $R·CR'H·CH_2·CH_2·OH$ and the Corresponding Acids, starting with Aldehydes, $R·COH$, and Ketones, $R·CO·R'$. A. VERLEY (*Bull. Soc. chim.*, 1924, [iv], **35**, 487—488).—Condensation of an aldehyde and a ketone in presence of sodium ethoxide gives rise to an ester of the type  $\overset{}{R·CH}\underset{O}{\diagdown\!\!-\!\!\diagup}CH·CO_2Et$, which, by reduction with sodium and alcohol, gives the alcohol, $CH_2R·CH_2·CH_2·OH$, and by hydrolysis followed by reduction, the acid $CH_2R·CH_2·CO_2H$. A. B. H.

Catalytic Decomposition of Ethyl Alcohol in the Presence of Alumina. J. E. GORIS (*Chim. et Ind.*, 1924, **11**, 449—452).—Ethyl alcohol is decomposed into ethylene and water when its vapour is passed over alumina heated at 430—450°; a small quantity of hydrogen (about 4·5% of the ethylene) is also produced, and the formation of hydrogen increases rapidly with increase of temperature above the limit mentioned. The volume of ethylene produced is a measure of the amount of alcohol, and the reaction may be used for the determination of alcohol in mixtures of alcohol and benzene, since the latter is not decomposed by the catalyst. To prepare the catalyst, a mixture of equal weights of aluminium hydroxide and pumice-stone is powdered and heated for 1 hour at 300°. W. P. S.

Chlorination of Ethyl Alcohol. F. D. CHATTAWAY and O. G. BACKEBERG (*J. Chem. Soc.*, 1924, **125**, 1097—1101).—The initial stage in the chlorination of ethyl alcohol consists in the formation of ethyl hypochlorite, which then reacts with the excess of alcohol to yield acetaldehyde. The latter undergoes a series of changes resulting in the successive formation of (*inter alia*) monochloroacetaldehyde alcoholate, trichloroethyl ether, dichloroacetaldehyde alcoholate, and finally chloral alcoholate. C. J. S.

Stepwise Oxidation of Citronellol and Geraniol. A. KOTZ and T. STECHE (*J. pr. Chem.*, 1924, [ii], **107**, 193—210; cf. Verley, A., 1919, i, 146).—The regulated oxidation of citronellol and geraniol yields formic acid, thus pointing to the presence of the group $CH_2{:}CMe$–. Citronellol, treated with perbenzoic acid (Prileschaeff, A., 1912, i, 633), gives *oxidocitronellol*, $C_{10}H_{20}O_2$, an oil, b. p. 139—140°/13 mm., d_4^{20} 0·9439, n_D^{20} 1·45519, in nearly theoretical yield. This product is rapidly hydrolysed by dilute sulphuric acid to dihydroxyhydrocitronellol, which, oxidised with ice-cold alkaline potassium permanganate solution, gives an oily substance, possibly *α-hydroxy-αε-dimethylsuberic acid*; the latter substance at 30° breaks up into formic acid and a heavy oil. Dihydroxyhydrocitronellol oxidised with cold chromic acid yields acetic acid, a little acetone, and β-methyladipic acid.

When geranyl acetate is oxidised in ice-cold solution with potassium permanganate, *dihydroxygeraniol oxide acetate*, m. p. 106—106·5°, is obtained, which is hydrolysed to *dihydroxygeraniol oxide*, m. p. 99°. The latter, treated with ice-cold potassium permanganate, gives an oily acid, possibly *αεζ-trihydroxy-αε-dimethylsuberic acid*, which at 30° rapidly breaks up into formic acid and a ketonic compound, yielding a *phenylhydrazone*, m. p. 166—167°. The same end-products were obtained by oxidising geraniol dioxide or geraniol itself in the same way. W. A. S.

Complex Compounds of Bivalent Platinum with Organic Disulphides and Polysulphides. L. Tschugaev and S. Iljin [Edited by E. Fritzmann] (*Z. anorg. Chem.*, 1924, **135**, 143—152).—*β-Dimethyltrimethylene diethyl dithioether*, $CMe_2(CH_2{\cdot}SEt)_2$, prepared by the action of sodium mercaptide on pentaglycol, when shaken for 3 hours with an aqueous solution of potassium chloroplatinate, gives an insoluble rose-coloured *powder*, $\left[C_9H_{20}\right]\begin{matrix}-S\\-S\end{matrix}{>}PtCl_2$, which reacts with salts of Rieset's base; on heating, it yields a yellow form, m. p. 218—219°, soluble in alcohol, giving no reaction with Rieset's salts, to which the structure $\left[(C_9H_{20})\begin{matrix}-S\\-S\end{matrix}{>}Pt{<}\begin{matrix}S-\\S-\end{matrix}(C_9H_{20})\right]PtCl_4$ is assigned.

Pentaerythrityl ethyl thioether, $C(CH_2{\cdot}SEt)_4$, b. p. 216—218°/14 mm., when shaken with the chloroplatinite solution in the cold yields a yellow insoluble *compound*, $PtCl_2{<}\begin{matrix}SEt{\cdot}CH_2\\SEt{\cdot}CH_2\end{matrix}{>}C{<}\begin{matrix}CH_2{\cdot}SEt\\CH_2{\cdot}SEt\end{matrix}$. If the reaction mixture is heated, a mixture is produced of this substance and a *compound*, $\left(PtCl_2{<}\begin{matrix}SEt{-}CH_2{-}\\SEt{-}CH_2{-}\end{matrix}\right)_2C$.

Acetylene diethyl dithioether, $SEt{\cdot}CH{:}CH{\cdot}SEt$, reacts very rapidly in the cold with potassium chloroplatinate solution, giving a rose-coloured powder which quickly changes to a yellow form. S. I. L.

Complex Compounds of Palladium with Organic Mono- and Di-sulphides. L. Tschugaev and C. Iwanov [Edited by E. Fritzmann] (*Z. anorg. Chem.*, 1924, **135**, 153—160).—The additive compounds of diethyl sulphide with palladium dichloride have been re-examined, and the descriptions of Ardell (*ibid.*, 1897, **14**, 143) and of Phillips (A., 1901, i, 444) confirmed except in the following particulars: $PdCl_2,2Et_2S$, m. p. 82°; $PdBr_2,2Et_2S$, m. p. 100°; $PdI_2,2Et_2S$, m. p. 104°. The solubilities in *iso*pentane at 25° have been determined.

With the ethylene diethyl dithioether, $SEt{\cdot}CH_2{\cdot}CH_2{\cdot}SEt$, an analogous series of compounds has been obtained. The *chloride*, $PdCl_2,C_6H_{14}S_2$, m. p. 180°, *bromide*, m. p. 159°, and *iodide*, m. p. 154°, exist in one form only.

The action of carbon monoxide on complex palladium compounds has been examined; whilst the ammoniacal compounds are readily reduced, the sulphide compounds are less readily and the disulphide compounds only with difficulty reduced; the speed of reduction varies with the solubility. S. I. L.

Application of Thallium Compounds in Organic Chemistry. I. Thallous Hydroxide. R. C. Menzies and E. M. Wilkins (*J. Chem. Soc.*, 1924, **125**, 1148—1152).—A standard solution of thallous hydroxide may be used for the titration particularly of organic acids. The thallous salts of organic acids are considerably less soluble than those of the alkali metals, are readily crystallised, and hence can be used as a convenient means of isolation and purification. Several new thallous salts are described. The *palmitate* (feathery aggregates from ethyl alcohol) and the *oleate* (white needles) both behave as soaps in dilute aqueous solution. Normal *thallous adipate*, crystalline leaflets, *normal pimelate*, long needles, and *hydrogen pimelate*, prisms, m. p. 137—140°, have also been prepared. The *thallous* salt of ethyl acetonedicarboxylate forms minute needles, m. p. 125° (decomp.). Thallous hydroxide dissolves isatin and yields yellow needles of *thallous isatate*, decomp. 148°.

Thallous hydroxide gives coloured solutions when heated with reducing sugars, thus resembling sodium hydroxide; further heating causes reduction with the formation of thallium mirrors. Non-reducing sugars are not affected. C. J. S.

Basic Zinc Acetate Analogous to the Beryllium Salt. V. AUGER and (MLLE.) I. ROBIN (*Compt. rend.*, 1924, **178**, 1546—1548).—Whereas the distillation of zinc acetate under atmospheric pressure or in a moderate vacuum furnishes the normal salt mixed with decomposition products, distillation in a high vacuum gives, in a pure state, the *basic* salt, $Zn_4O(CH_3CO_2)_6$, which crystallises in transparent octahedra, m. p. 249—250°, decomposed by water and by absolute alcohol. Urbain and Lacombe (A., 1902, i, 132) obtained the corresponding salt of beryllium, and the formation of this volatile basic zinc salt demonstrates the close analogy between beryllium and zinc (cf. Lacombe, A., 1902, i, 418).
J. W. B.

Heterogeneous Catalysis. I. Selective Action of the Nickel Catalyst in the Hydrogenation of certain Vegetable Oils. A. S. RICHARDSON, C. A. KNUTH, and C. H. MILLIGAN (*Ind. Eng. Chem.*, 1924, **16**, 519—522).—The hydrogenation of cotton seed, arachis, and soya bean oils is characterised by the preferential conversion of linoleic acid to oleic acid and its isomerides. The selective hydrogenation of linoleic acid appears to be more marked when increasing amounts of the nickel catalyst are used and when the temperature is increased up to an optimum of about 200°. It appears to be well established that the normal course of hydrogenation of a single unsaturated component of a liquid mixture involves a constant rate of hydrogen absorption as long as the concentration of that component exceeds a fairly well-defined critical value. Owing to the selective action of the catalyst, a constant rate of hydrogen absorption is not uncommon, even when the reaction mixture contains a variety of unsaturated components. H. C. R.

Catalytic Hydrogenation of Oleic Acid and Commercial Olein with Nickel as Catalyst. DE ROUBAIX (*Bull. Soc. chim. Belg.*, 1924, **33**, 193—212).—Oleic acid and commercial olein may be completely hydrogenated, after purification by distillation under diminished pressure, by means of a rapid current of hydrogen at atmospheric pressure in the presence of 4% of reduced nickel as catalyst, the temperature being between 160° and 230°. The catalyst should not be prepared within the material to be hydrogenated, as this leads to considerable formation of nickel oleate, which encloses the nickel particles and inhibits their action. The presence of sulphur in non-distilled olein poisons the catalyst. [Cf. *B.*, July 25th.] W. T. K. B.

Preparation of Solutions of Acetoacetic Acid. G. Ljunggren (*Biochem. Z.*, 1924, **145**, 422—425).—A 2% excess of sodium hydroxide solution warmed to 25° is placed in a flask which has been blown out with air free from carbon dioxide, and a weighed quantity of methyl acetoacetate is added. Hydrolysis is complete in 250 minutes and the solution is then neutralised with hydrochloric acid or by passing a stream of carbon dioxide for 10 minutes. The solution is 0·3% less concentrated than theory demands. The methyl alcohol resulting from the hydrolysis may be removed by aëration in a vacuum with pure air. Under similar conditions, ethyl acetoacetate is hydrolysed in 375 minutes. Kept over ice, such solutions decrease in concentration by 0·15% *per diem.* J. P.

Pyrogenic Dissociation of Sodium Oxalate. S. Ott (*Z. physikal. Chem.*, 1924, **109**, 1—33).—The thermal decomposition of sodium oxalate, obtained by heating sodium formate, into sodium carbonate and carbon monoxide has been studied. At all temperatures at which an appreciable decomposition takes place, even as low as 160°, there is a further reaction by which the carbon monoxide gives carbon dioxide and carbon, which accelerates the further evolution of gas. Hydrogen always appears in the residual gases, probably derived from traces of water which are difficult to remove from the oxalate. The equilibrium pressure has not been reached experimentally in a single case. Heating sodium carbonate under a pressure of 1100 atmospheres of carbon monoxide (which is greatly in excess of the calculated pressure) failed to reverse the process. This result seems to indicate that the decomposition of sodium oxalate by heat is still another example of an irreversible equilibrium. M. S. B.

Stereochemistry of Ruthenium. R. Charonnat (*Compt. rend.*, 1924, **178**, 1279—1282).—Complex salts of ruthenium have been studied on the basis of the Werner theory of co-ordination. The compound $2[Ru(C_2O_4)_3]K_3,KCl,8H_2O$, which is perfectly hexa-co-ordinated, was prepared by treating $RuCl_3,HCl,2H_2O$ with a slight excess of normal potassium oxalate for 2 hours at 130°. By recrystallisation from water, the salt, $[Ru(C_2O_4)_3]K_3,4·5H_2O$, was obtained. These compounds are isomorphous with corresponding compounds of iridium and rhodium. Resolution was attempted by crystallisation of the double salt with *d*-potassium [illegible]. The active ruthenotrioxalate, however, either [illegible] immediately on liberation or possessed nearly zero rotatory power. The compound [Ru(NO) $en_2I]I_2,2H_2O$ was transformed by prolonged heating into a salt of the same molecular composition, but crystallising in the anhydrous form. This compound and the series derived from it must possess the *cis* configuration if the series prepared by Werner and Smirnoff (A., 1921, i, 13) possesses the *trans* configuration. A. B. H.

Stereochemistry of Ruthenium. R. CHARONNAT (*Compt. rend.*, 1924, **178**, 1423—1426; cf. preceding abstract).—The action of normal potassium oxalate (2 mols.) on Joly's salt, $[Ru(NO)Cl_5]K_2$, yields a highly soluble *potassium ruthenochloronitrosodioxalate*, $[Ru(NO)Cl(C_2O_4)_2]K_2$, which is prone to supersaturation and with alkaloids forms salts incapable of crystallising. The replacement of an atom of chlorine in the complex anion by a molecule of pyridine lowers the solubility and yields a more tractable compound. *Potassium ruthenonitrosopyridinodioxalate*, $[Ru(NO)C_5H_5N(C_2O_4)_2]K$, prepared by the successive action of potassium oxalate and pyridine on $[Ru(NO)Cl_5]K_2$, forms large, red, triclinic plates ($+4H_2O$), and by hydrochloric acid at 100° is converted into the complex $[Ru(NO)C_5H_5NCl_4]$. The latter, under the action of pyridine, gives the compound $[Ru(NO)(C_5H_5N)_2Cl_2(OH)]$, and this yields the compound $[Ru(NO)(C_5H_5N)_2Cl_3]$ (I), when treated with hydrochloric acid. Compound (I) is obtained also by the action of hydrochloric acid on the compound $[Ru(NO)(C_5H_5N)_2Cl(C_2O_4)]$, which is another product of the action of potassium oxalate and pyridine on the salt $[Ru(NO)Cl_5]K_2$. All these compounds are highly stable.

By double decomposition with quinine hydrochloride, potassium ruthenonitrosopyridinodioxalate yields two isomeric, pink quinine salts of different solubilities, the one dextro- and the other lævorotatory; the quinidine salts behave similarly, but most of the alkaloids yield uncrystallisable salts. In aqueous solution, the corresponding ammonium salts have $[\alpha]_D$ ±425°, and from a solution containing a mixture of the two a crystalline racemic salt may be obtained. The active pyridine salts were also obtained crystalline. T. H. P.

Condensation Reactions involving Elimination of Ester Groups. L. SOUTHER (*J. Amer. Chem. Soc.*, 1924, **46**, 1301—1305).—Methylene iodide condenses with methyl and ethyl phenylmalonates in presence of sodium methoxide with formation, respectively, of *methyl αγ-diphenylglutarate*, b. p. 205—210°/6 mm., and *ethyl αγ-diphenylglutarate*, b. p. 216—217°/7 mm., and elimination of methyl and ethyl carbonates. A new *isomeride* of αγ-diphenylglutaric acid, m. p. 185—186·5°, together with the ordinary modification, was obtained by saponification of the methyl ester with sodium methoxide. With ethyl phenylcyanoacetate, methylene iodide yields similarly αγ-diphenylglutaronitrile. F. G. W.

Rotatory Dispersion of Tartaric Acid. L. LONGCHAMBON.—(See ii, 373.)

Decomposition of Dihydroxymaleic Acid. A. Locke (*J. Amer. Chem. Soc.*, 1924, **46**, 1246—1252).—An attempted synthesis of optically active sugars by the decomposition of the quinine salt and menthyl ester of dihydroxymaleic acid failed because the rate of polymerisation of the glycollaldehyde first formed was so slow in comparison with that of the decomposition of the dihydroxymaleic acid that the orientating effect of the quinine and menthol was lost. An attempt to catalyse the condensation of the aldehyde by means of alkalis showed that the sodium and potassium salts of dihydroxymaleic acid are relatively stable in solution, and that the addition of pyridine induces rapid decomposition of the otherwise stable solution of dihydroxymaleic acid in chloroform or benzene. The rates of decomposition of dihydroxymaleic acid and its disodium salt were measured in aqueous solution at 25°, by determining at intervals the glycollaldehyde produced. The experimental values for the unimolecular constant of the reaction are in accordance with the hypothesis that decomposition proceeds through the solvated, non-ionised, carboxyl group.

F. G. W.

Biological Oxidation. I. Absorption of Oxygen by the System Linoleic Acid–SH Group. A. von Szent-Györgyi (*Biochem. Z.*, 1924, **146**, 245—253).—The product resulting from the catalytic oxidation of linoleic acid by thioglycollic acid in the presence of oxygen has been isolated as a dark yellow, viscous oil, which appears to be a compound of the ethylene oxide type, and not a peroxide, as supposed by Meyerhof (*Pflüger*, 1923, **199**, 531).

J. P.

Biological Oxidation. II. Mechanism and Significance of SH-Catalysis. A. von Szent-Györgyi (*Biochem. Z.*, 1924, **146**, 254—258).—From a comparison of the oxidative action of thioglycollic acid and of ethyl peroxide on various aliphatic acids in the presence of air and an iron catalyst, it is concluded that thioglycollic acid combines with the oxygen of the air to form an active peroxide.

J. P.

***n*-α-Sulphobutyric Acid and its Optically Active Components.** H. J. Backer and J. H. de Boer (*Rec. trav. chim.*, 1924, **43**, 297—315).—An extended account of work previously published in an abbreviated form (A., 1923, i, 536). *Lead α-sulphobutyrate* crystallises in small needles with $2H_2O$; a *basic* salt has the composition $C_4H_6O_5SPb_2(OH)_2$. *Copper α-sulphobutyrate* forms a pale blue crystalline powder containing $1H_2O$; the *copper hydrogen*, *nickel*, and *cobalt* salts are also described. Two *strychnine* salts are described, the *normal* salt, small, glistening needles, m. p. 226—227°, and the *hydrogen* salt, aggregates of small, white needles. The two corresponding *brucine* salts and the normal *quinine* salt were obtained. Both the strychnine and quinine salts were used [illegible] the resolution of α-sulphobutyric acid, the former depositing [illegible] salt of the *d*-acid, whilst the latter deposited the salt of [illegible] excess. The pure components of α-sulphobutyric acid have $[\alpha]_D$ ±7·8° and the normal barium salts, ±29·6°. The acid salts, in which the carboxyl group is probably free, have the same sign of rotation as the free acids, the value being about ±4°. The rotation-dispersions of the acid and its salts are normal, except for the coloured salts in alcohol. E. H. R.

Condensation of Aldehydes with Ammonia in Presence of Alumina. A. E. TSCHITSCHIBABIN (*J. pr. Chem.*, 1924, [ii], **107**, 129—131).—Further details of work already published (this vol., i, 312). W. A. S.

Sodium Hydroxylaminesulphonate as a Reagent for the Preparation of Oximes. W. L. SEMON and V. R. DAMERELL (*J. Amer. Chem. Soc.*, 1924, **46**, 1290—1293).—Sodium hydroxylaminemonosulphonate forms a convenient reagent for the preparation of oximes in acid solution. The ketone is heated at 70—100° with the theoretical quantity of the sodium monosulphonate in aqueous solution (1·29 mols. per litre), made alkaline in the cold, and the oxime extracted with a solvent. Negative results were obtained with benzil and quinonemonoxime. F. G. W.

Reduction of Citronellal. H. RUPE and R. RINDERKNECHT (*Helv. Chim. Acta*, 1924, **7**, 541—546).—Citronellal was reduced by von Braun and Kaiser (this vol., i, 3) to dihydrocitronellol ($\gamma\eta$-dimethyloctanol), $[\alpha]_D$ +2·38°, a value only about one-half that of citronellol, $[\alpha]_D$ +4·17°. This contradicts the authors' rule that a double bond so far removed from the asymmetric carbon atom as that in citronellol should have practically no effect on the rotation. The authors have therefore repeated the reduction of citronellal, using the nickel catalyst previously described (A., 1919, i, 29). The dihydrocitronellol had n_D 1·43417, $[\alpha]_D$ +4·09°, from which it is concluded that the preparation of von Braun and Kaiser, obtained by reduction under pressure at 150°, was impure. Both citronellol and dihydrocitronellol show slightly anomalous rotation dispersion. E. H. R.

Carbohydrates and Polysaccharides. IX. Synthesis of 2 : 3-Dimethyl*cyclo*pentenaldehyde. R. R. READ and H. HIBBERT (*J. Amer. Chem. Soc.*, 1924, **46**, 1281—1283).—β-*Bromobutaldehyde diethyl acetal*, $CHMeBr\cdot CH_2\cdot CH(OEt)_2$, a heavy, yellow, unstable oil, b. p. 82—85°/12—15 mm., was obtained by the addition of crotonaldehyde to alcoholic hydrobromic acid. This was treated with magnesium in ether, and the product decomposed with dilute sulphuric acid. The oil obtained was identical with the 2 : 3-dimethyl*cyclo*pentenaldehyde obtained by the electrolytic reduction of crotonaldehyde (this vol., i, 613). Its formation is to be represented by the elimination of water from dimethyladipaldehyde, the acetal of which is formed by the elimination of bromine from two molecules of β-bromobutaldehyde diethyl acetal by the action of the magnesium. A similar synthesis could not be carried out with the corresponding chlorine compound. F. G. W.

Carbohydrates and Polysaccharides. X. Synthesis and relative Stability of Cyclic Acetals from αβ- and αγ-Glycols. H. Hibbert and J. A. Timm (*J. Amer. Chem. Soc.*, 1924, 46, 1283—1290).—The relative stability and ease of formation of 5- and 6-membered cyclic acetals were measured by allowing an αβ- and an αγ-glycol to condense competitively with various aldehydes in presence of dilute sulphuric acid at 100°, and measuring the yields of the two cyclic acetals formed when equilibrium had been reached. In the cases examined, the end-product contained a preponderance of the 6-membered derivative, the preponderance being greater the higher the molecular weight of the aliphatic aldehyde employed. A mixture of ethylene and trimethylene glycols (1 mol. of each) condensed with 1 mol. of paracetaldehyde, *n*-butaldehyde, *n*-heptaldehyde, and benzaldehyde, respectively, to form the 5- and 6-membered cyclic acetals in the respective proportions 1 : 1·8, 1 : 6·6, 1 : 7·3, and 1 : 2·1. Similar partition experiments, using ethylene glycol (1 mol.) and a mixture of benzaldehyde (1 mol.) with paracetaldehyde, *n*-butaldehyde, or *n*-heptaldehyde (1 mol.) gave ratios of the yields of products from benzaldehyde to those from the aliphatic aldehydes of 1 : 3·6, 1 : 1·2, and 1 : 0·7, respectively. Using trimethylene glycol, the corresponding ratios were 1 : 6·2, 1 : 4·4, and 1 : 2·0, the stability of cyclic acetals from aliphatic aldehydes decreasing with increasing molecular weight. The n-*butylidene ether*, b. p. 132—136°, and *benzylidene ether*, b. p. 225°, of ethylene glycol and the n-*butylidene ether*, b. p. 154—157°, of trimethyleneglycol are described. The cyclic acetals are readily hydrolysed by water or dilute acids, are more stable to alkalis, and very resistant to permanganate in acetone.

F. G. W.

Application of Azeotropy to the Preparation of Organic Compounds. H. Wuyts (*Bull. Soc. chim. Belg.*, 1924, 33, 167—192).—A general discussion of the vapour pressures and boiling points of liquid binary mixtures, and a recapitulation of previous work on esterification (A., 1921, i, 494) and etherification (A., 1923, i, 532). Similar methods are described for the preparation of formals. In each case, the lower members of the homologous series are obtained directly as the most volatile component or as the predominant constituent of a binary mixture. With the higher members, the separation is facilitated by the heterogeneity of the mixture, and water is eliminated in the form of a binary mixture with alcohol.

W. T. K. B.

Preparation of Acetals from Aldehydes and Ketones. B. Helferich and J. Hausen (*Ber.*, 1924, 57, [*B*], 795—799).—Acetals may be obtained by the action of orthosilicic esters (1·1 mols.) on solutions of aldehydes or ketones (1 mol.) in the requisite anhydrous alcohol (2—3 mols.) in the presence of hydrogen chloride; [illegible] mixtures are preserved for some days at the atmospheric tem[illegible] heated under a reflux condenser. Unchanged ester is [illegible] by treating the products with potassium [illegible] new method is not more advantageous than

Fischer's process in those cases in which the latter gives good yields, but is superior to that involving orthoformic esters, since the materials are more readily prepared, and, in certain cases, it is possible to transform unsaturated aldehydes and ketones into acetals without addition of alcohol at the double bond. The following compounds are described: lævulinaldehyde (keto)-dimethylacetal, b. p. 76—80°/10 mm., d_4^{20} 0·9713, n_D^{20} 1·4203; the derivatives of *cyclo*hexanone: *dimethylacetal*, b. p. 54—56°/13 mm., $d_4^{19\cdot2}$ 0·9528, $n_D^{19\cdot2}$ 1·4416; *diethylacetal*, b. p. 75—76°/13 mm., $d_4^{17\cdot5}$ 0·9156, $n_D^{17\cdot5}$ 1·4452; *diallylacetal*, b. p. 106—108°/13 mm., $d_4^{17\cdot5}$ 0·9410, $n_D^{17\cdot5}$ 1·4632; *diisobutylacetal*, b. p. 115—116°/13 mm., d_4^{15} 0·8927, n_D^{15} 1·4413; *diisoamylacetal*, b. p. 138—140°/12 mm., $d_4^{18\cdot5}$ 0·9165, $n_D^{18\cdot5}$ 1·4605; *benzaldehyde cetylacetal*; *crotonaldehyde dimethylacetal*, b. p. 124—128°/760 mm., d_4^{18} 0·8829, n_D^{18} 1·4130; *methylheptenone dimethylacetal*, b. p. 80—83°/14 mm., d_4^{18} 0·8770, n_D^{18} 1·4380.

The requisite orthosilicic esters are prepared by gradually adding silicon tetrachloride (1 mol.) to the well-cooled alcohol (4·4 mols.) and subsequently slowly heating the mixture to its boiling point if this does not exceed 150° and keeping it at this temperature until hydrogen chloride ceases to be evolved. The final traces of acid are removed by treatment of the product with a solution of sodium ethoxide in alcohol. The following new esters are described: *tetra-allyl orthosilicate*, b. p. 115—116°/13 mm., d_4^{17} 0·9842, n_D^{17} 1·4347; *tetrabenzyl orthosilicate*, long needles, m. p. 32·5°, b. p. 305°/12 mm.; *tetra*cyclo*hexyl orthosilicate*, needles, m. p. 88·5°, b. p. 230—240°/11 mm.; *tetra-acetyl orthosilicate*, m. p. 46·5—48·5°. Tetramethyl, tetraethyl, tetra*iso*butyl, and tetra*iso*amyl orthosilicates have b. p. 25—27°/12 mm., 60—62°/12 mm., 129—131°/13 mm., and 173—176°/12 mm., respectively. *Methyl silico-orthoformate*, b. p. 104—106°/760 mm., is prepared in 66% yield from methyl alcohol and trichlorosilane.

H. W.

Additive Products of Methyl Ethyl Ketone with Chloroform, Bromoform, and Iodoform. B. EKELEY and C. J. KLEMME (*J. Amer. Chem. Soc.*, 1924, **46**, 1252—1254).—Chloroform, bromoform, and iodoform (2 mols.) condense, respectively, with methyl ethyl ketone (1 mol.) in presence of dry, powdered potassium hydroxide, with formation of *trichloro*-tert.-*amyl alcohol*, b. p. 110—113°/620 mm. (decomp.), d_4^{20} 1·2128, n_D^{20} 1·4460, M_D 42·107; *tribromo*-tert.-*amyl alcohol*, b. p. 130—135°/40 mm. (decomp.), d_4^{20} 1·8788, n_D^{20} 1·5130, and *tri-iodo*-tert.-*amyl alcohol*, d_4^{20} 2·1438, n_D^{20} 1·5680. The products are yellow, pungent liquids, which produce a numbing sensation when placed on the tongue. The first two, but not the last, are fairly stable in the dark, and they are all less stable than the corresponding trihalogeno-*tert*.-butyl alcohols.

F. G. W.

Comparison of Hydrogen Ion and Enzyme Catalysis of certain Sugars and Glucosides. R. KUHN and H. SOBOTKA (*Z. physikal. Chem.*, 1924, **109**, 65—76).—In the enzymic hydrolysis of sugar derivatives an enzyme–sugar compound is formed as an intermediate product (cf. Kuhn, A., 1923, i, 1033). It has been found (unpublished work) that the rates of enzyme hydrolysis of α-phenylglucoside, α-methylglucoside, and maltose vary as the corresponding rates of acid hydrolysis, and similar relations hold for raffinose and sucrose, but not for helicin, salicin, and β-methyl- and β-phenyl-glucosides. Various reasons are suggested to account for the difference, including the possibility that it may be due to the large differences between the acid dissociation constants of the different glucosides. Experiments have therefore been made to determine the influence of the hydrogen-ion concentration on the dissociation constant of the emulsin–salicin compound in the hydrolysis of salicin by emulsin. The maximum activity of the enzyme is obtained at p_H 4·4, and falls to half value at p_H 6·8. The concentration of salicin at which the activity is half the maximum, increases from 0·035*N* for p_H 4·4 to 0·047*N* for p_H 6·8. According to Michaelis and Rothstein (A., 1920, i, 896), it should, on the contrary, fall to half. The salicin–emulsin compound is to be regarded as half dissociated at these concentrations of salicin, that is, the dissociation constants are 0·035 at p_H 4·4 and 0·047 at p_H 6·8.

The acid dissociation constants of a number of sugars and glucosides have also been determined, and several differ to a rather large extent from those found by Michaelis and Rona (A., 1913, ii, 379).

M. S. B.

Stepwise Oxidation of Dextrose. M. Hönig and F. Tempus (*Ber.*, 1924, 57, [*B*], 787—791).—Cautious oxidation of dextrose by means of cold barium hypobromite, in presence of a slight excess of barium hydroxide, effects a stepwise oxidation in which the chief products are gluconic acid, β-ketogluconic acid, and arabonic acid, using 1, 2, or 3 equivalents of oxygen, respectively. Further oxidation affords a complex mixture of various substances such as arabonic, saccharic, tartaric, formic, and acetic acids. The constitution of ketogluconic acid was shown by its degradation by carboxylase to *d*-arabinose. Ketogluconic acid was identified by its *calcium* salt, [α] −9·56°, and *osazone*, bright yellow needles, m. p. 174°.

F. A. M.

Polysaccharides. XXVI. Cleavage of Lichenin into Dextrose. P. Karrer and M. Staub (*Helv. Chim. Acta*, 1924, 7, 518—519).—The quantitative conversion of lichenin (reserve cellulose) into dextrose by lichenase (cf. A., 1923, i, 1182) has been confirmed by the preparation of the crystalline sugar in almost quantitative yield from the fermented lichenin solution.

E. H. R.

Acetone [*iso*Propylidene] Compounds of the Mercaptals of certain Monosaccharides. I. Acetone Compounds of *d*-Glucosedibenzylmercaptal. E. Pacsu (*Ber.*, 1924, 57, [*B*], 849—853).—*d*-Glucosedibenzylmercaptal, $[\alpha]_D^{15}$ −98·37° in pyridine, [illegible] (Lawrence, A., 1896, i, 272, gives m. p. 133°), con- [illegible] acetone to form a brown syrup which was separated [illegible] chloroform and light petroleum into the crystalline *monoacetone*-d-*glucosedibenzylmercaptal*, m. p. 94°, $[\alpha]_D^{15}$ $-16{\cdot}44°$ (in tetrachloroethane), and the yellow, syrupy *diacetone*-d-*glucosedibenzylmercaptal*, which was treated with *p*-toluenesulphonyl chloride in pyridine to give p-*toluenesulphonyldiacetone*-d-*glucosedibenzylmercaptal*, colourless needles, m. p. 114°, $[\alpha]_D^{15}$ $-51{\cdot}89°$ (in tetrachloroethane). The crude mixture of *iso*propylidene dimercaptal was converted by methylation and subsequent hydrolysis of the product into *monomethyl*-d-*glucosedibenzylmercaptal*, colourless needles, m. p. 190—191°, $[\alpha]_D^{15}$ $-109{\cdot}02°$ in pyridine, and *trimethyl*-d-*glucosedibenzylmercaptal*, $C_6H_5(OH)_4(OMe)(S{\cdot}CH_2Ph)_2$, hexagonal platelets, m. p. 73—74°, $[\alpha]_D^{15}$ $-63{\cdot}12°$ in pyridine. F. A. M.

Synthetic Action of α-*d*-Mannosidase in the Presence of some Monohydric Alcohols. H. HÉRISSEY and J. CHEYMOL (*Bull. Soc. Chim. biol.*, 1924, **6**, 186—189).—The action on mannose of α-*d*-mannosidase from lucerne grains (A., 1913, i, 497) in the presence of ethyl, propyl, *iso*propyl, or *n*-butyl alcohol results in the synthesis of the corresponding α-mannoside. J. P.

Isolation of Sucrose from Mixtures of Dextrose, Lævulose, and Sucrose. S. KOMATSU and M. TANIMURA (*Mem. Coll. Sci., Kyōtō*, 1924, **7**, 161—163).—Sucrose was isolated in the crystalline state from mixtures with lævulose and dextrose after transforming the reducing sugars into the sugar acids by oxidation with yellow mercuric oxide in the presence of calcium carbonate. The solution was kept neutral in order to reduce the hydrolysis of the sucrose. The sucrose was then crystallised from glacial acetic acid.

H. C. R.

Oxidation of Lævulose in Phosphate Solutions. O. WARBURG and M. YABUSOE (*Biochem. Z.*, 1924, **146**, 380—386).—In the presence of phosphates lævulose, but not dextrose, is oxidised by molecular oxygen with the formation of ⅓ mol. of carbon dioxide per mol. of oxygen absorbed. The rate of oxidation, which is most rapid during the first few hours, then slowly decreases; it increases with increasing p_H, and with the phosphate and lævulose concentration, other factors being kept constant. The phosphate cannot be replaced by other salts, and its action is regarded as specific.

J. P.

Reaction of Acetohalogen-sugars with Tertiary Bases. P. KARRER, A. WIDMER, and J. STAUB (*Helv. Chim. Acta*, 1924, **7**, 519—527; cf. A., 1921, i, 766).—By the action of trimethylamine on acetobromocellobiose a substance is obtained having the composition $C_{12}H_{14}O_{10}Ac_6$, long, white needles, m. p. 206°, $[\alpha]_D$ $-11{\cdot}3°$, to which the name *cellal acetate* is given. It cannot be hexa-acetylanhydrocellobiose, since it reduces Fehling's solution (in presence of alcohol or pyridine as solvent) and is quite stable to acids. By vigorous treatment with acetic anhydride and sodium acetate, it gives octa-acetylcellobiose. Unlike the latter compound, it is not converted into aceto-αζ-dibromoglucose by phosphorus pentabromide.

The tetra-acetylglucosidopyridinium bromide of Fischer and Raske is hydrolysed by dilute hydrobromic acid to *glucosidopyridinium bromide*, m. p. 179°, $[\alpha]_D$ +41·4°; the corresponding *chloride* has m. p. 177°, $[\alpha]_D$ +49·2°, the *iodide*, m. p. 183°, and the *perchlorate*, m. p. 170°. The fact that the pyridinium salt does not give lævoglucosan when hydrolysed with alkali, and that the acetyl compound has a negative rotation, suggests that the pyridinium salt has an α-configuration, whilst tetra-acetylglucosidotrimethylammonium salts (A., 1921, i, 766) have the β-configuration.

When ζ-bromotriacetyl-β-methylglucoside is heated with trimethylamine, *methylglucosidotrimethylammonium bromide*, white crystals which darken at 240°, m. p. 263—266° (decomp.), is obtained; the *chloride* has m. p. 274—275° (decomp.); *perchlorate*, broad needles, m. p. 125°; *picrate*, microcrystalline; *chloroaurate*, m. p. 136°. Extensive decomposition occurs when the salts are heated with alkali. E. H. R.

Absorptive Power of Starch for Gases and its Action on Magnesium Alkyl Derivatives. D. Costa (*Gazzetta*, 1924, **54**, 207—211).—The action of magnesium ethyl bromide on starch in ethereal solution and in complete absence of moisture (cf. A., 1923, i, 186) yields a grey, granular *compound*, $C_6H_9O_5{\cdot}MgBr,Et_2O$.

Under similar conditions, starch absorbs about twice as much hydrogen chloride (above 18·55%) as does cellulose (cf. Oddo, A., 1920, i, 16) and undergoes transformation into a black substance completely soluble in water. Ammonia and sulphur dioxide also are absorbed by starch in the proportion of approximately 1 mol. per $C_6H_{10}O_5$, the starch undergoing no apparent change. Starch absorbs about 0·675% (or 0·065%) of its weight of carbon dioxide (or oxygen). T. H. P.

Starch. IX. Constitution of the Polyamyloses. H. Pringsheim and J. Leibowitz (*Ber.*, 1924, **57**, [*B*], 884—887; cf. A., 1923, i, 899).—By treatment of α-tetra-amylose or β-hexa-amylose with cold concentrated hydrochloric acid according to the method of A. and J. Pictet (A., 1923, i, 755) the authors have obtained a new disaccharide, termed *amylobiose*, $C_{12}H_{22}O_{11}$, which retains in its molecule the second bond of the glucose portion of diamylose, contrary to the views of Karrer and co-workers (A., 1922, i, 435). It is a pure white powder, $[\alpha]_D^{20}$ +138° in water (*osazone*, m. p. 189°). Amylobiose remained unattacked by maltase or emulsin, but was fermented by amylase; it is suggested that amylobiose is a glucosido-γ-glucose. F. A. M.

Starch. X. Different Structures of the Two Constituents of Starch. H. Pringsheim and K. Wolfsohn (*Ber.*, 1924, **57**, [*B*], 887—891; cf. A., 1923, i, 899, and preceding abstract).—The view of Pringsheim and Goldstein (A., 1923, i, 899) that the content- and integument-substances of the starch granule contain respectively a disaccharide and a trisaccharide has now been confirmed directly. Starch paste was separated into amylose and amylopectin, by the method of Ling and Nanji (T., 1923, **123**,

2666) and the two substances were depolymerised separately by acetylation (cf. Pringsheim and Eissler, A., 1913, i, 1156) and by heating to 200—210° in glycerol (cf. Pictet and Jahn, A., 1922, i, 987), with the addition of a small quantity of phosphoric acid. Acetylation of amylopectin with acetic anhydride and sulphuric acid gave an *acetate*, $C_{36}H_{48}O_{24}$, $[\alpha]_D^{20}+143\cdot6—144\cdot2°$ in tetrachloroethane, whilst the *acetate* of *amylose*, $C_{24}H_{32}O_{16}$, had $[\alpha]_D^{20}+142\cdot4—142\cdot8°$ in tetrachloroethane. Depolymerisation of amylopectin in glycerol gave a *trihexosan*, $C_{18}H_{30}O_{15}$, $[\alpha]_D^{20}+165\cdot2—167\cdot5°$ in water, whilst amylose gave a dihexosan, $C_{12}H_{20}O_{10}$, $[\alpha]_D^{20}+153\cdot9—154\cdot8°$ in water. The product obtained by Pictet and Jahn (*loc. cit.*) of $[\alpha]_D$ $+162\cdot2°$ was therefore a mixture of trihexosan and dihexosan.

F. A. M.

Behaviour of Cellulose and Lignin during Decay. F. Fischer (*Brennstoff-Chem.*, 1924, 5, 132—133).—The work of Bray and Andrews (*Ind. Eng. Chem.*, 1924, **16**, 137) on the chemical processes during the bacterial decay of wood is cited in support of the author's hypothesis that the origin of coal is not principally the cellulose of dead vegetation but the lignin. Those authors showed that in the space of three years the cellulose calculated on the original wood had decreased down to 6·05%, whereas the lignin had practically resisted. Schwalbe's experiments whereby he prepared a substance resembling coal by the action of powerful dehydrating agents on cellulose are not held to be valid in determining the origin of coal because the conditions were so different from those prevailing in nature. It is far more probable that dead vegetation would be rapidly attacked by bacterial decay, with consequent destruction of the cellulose, than that it should be preserved and converted into coal by the accidental occurrence of powerful dehydrating conditions. J. F. B.

Conversion of Ligneous Plant Substances into Coal. II. Chemical Composition and Properties of Coal-like Substances from Cellulose. C. G. Schwalbe and R. Schepp (*Ber.*, 1924, 57, [*B*], 881—883; cf. this vol., i, 377).—Analytical figures are given for the composition of the coal-like substances obtained by heating wood-cellulose with concentrated solutions of salts during various periods. The artificial product appears to be more closely related to the lignites than to ordinary coal or to the humic acids, which was shown by analysis and by the behaviour both with alkalis and with nitric acid; there are, however, also very distinct differences in general behaviour between lignite and the artificial coal.

F. A. M.

Isomorphism of the Amides and Substituted Amides of Dichloro- and Chloroiodo-acetic Acids, and of Chlorobromo- and Chloroiodo-acetic Acids. [Miss] P. V. McKie (*J. Chem. Soc.*, 1924, **125**, 1075—1079).—The fusion mixtures of corresponding pairs of the amides and substituted amides of dichloro- and chloroiodo- and of chlorobromo- and chloroiodo-acetic acids show isomorphism (cf. T., 1923, **123**, 2213). In the corresponding series of derivatives of dichloro- and chlorobromo-acetic acids the melting-point curve approximates to a straight line joining the melting points of the two components of each system, whereas the curves of pairs of derivatives of chlorobromo- and chloroiodo-acetic acids diverge from the straight line, the effect being very marked with derivatives of dichloro- and chloroiodo-acetic acids. The following compounds were prepared by methods similar to those previously employed (*loc. cit.*): *Chloroiodoacetomethylamide*, m. p. 117·5°; *chloroiodoacetoethylamide*, m. p. 79·4°; *chloroiodoacetobenzylamide*, m. p. 120·5°; *chloroiodoacetomethylanilide*, m. p. 88·0°; *chloroiodoacetoethylanilide*, m. p. 92·3°. C. J. S.

Alkylchloromalonamides. Influence of Homology on Taste. A. W. Dox and B. Houston (*J. Amer. Chem. Soc.*, 1924, **46**, 1278—1281).—Ethylchloromalonamide was obtained by the action of sulphuryl chloride on ethylmalonamide. Dichloromalonamide and the following alkylchloromalonamides were prepared by the action of chlorine on the appropriate malonamides in glacial acetic acid solution. *Methyl-*, m. p. 224—225°; *ethyl-*, m. p. 135°; n-*propyl-*, m. p. 150°; n-*butyl-*, m. p. 136°; iso*butyl-*, m. p. 132°; iso*amyl-*, m. p. 157°; n-*hexyl-*, m. p. 130°; and *benzylchloro-malonamide*, m. p. 183—185°. *iso*Propylmalonamide could not be chlorinated directly, and iso*propylchloromalonamide*, m. p. 177°, was obtained by the action of ammonia on *methyl* iso*propylchloromalonate*, a colourless oil, b. p. 110—112°/37 mm., 221—222°/757 mm., prepared by the chlorination of methyl *iso*propylmalonate. All the *n*-alkylchloroamides, as well as mono- and di-chloromalonamides, are sweeter than sucrose, the *n*-butyl derivative being at the same time bitter. The *iso*alkyl derivatives are bitter. Constant differences in sweetness between succeeding members of the series could not be established. F. G. W.

Derivatives of Semioxamazide. II. F. J. Wilson and E. C. Pickering (*J. Chem. Soc.*, 1924, **125**, 1152—1156).—In addition to the ketonic semioxamazones previously described (T., 1923, **123**, 394) others have been obtained by the same method. *Methyl* n-*hexyl ketone semioxamazone*, $C_6H_{13}\cdot CMe{:}N\cdot NH\cdot CO\cdot CO\cdot NH_2$, forms small, colourless needles, m. p. 115—116°. *Benzil monosemioxamazone*, long, colourless prisms, m. p. 181—182°. *Benzil disemioxamazone* is a white powder, m. p. 275—278° (decomp.). *Dibenzyl ketone semioxamazone* is dimorphic, colourless prisms, m p. 195—196°, being deposited from alcohol above 40°, whilst at temperatures below this, and from more dilute solutions, it crystallises in colourless needles, m. p. 187—189°.

Benzylamine and semioxamazide interact on heating to form *s*-dibenzyloxamide hydrazone, hydrazine, and ammonia. Benzylamine and acetophenone semioxamazone, when heated at 150°, gave *s*-dibenzyloxamide, methylphenylketazine m. p. 129—130°, hydrazine, and ammonia. Benzylamine and dibenzyl ketone semioxamazone react similarly to give *s*-dibenzyloxamide and *dibenzylketazine*, m. p. 95—96°, which has also been synthesised by [illegible] dibenzyl ketone and hydrazine hydrate in a sealed tube at

100°. By the interaction of piperidine and acetophenone semioxamazone there results *acetophenone piperidino-oxalylhydrazone*, a white, microcrystalline powder, m. p. 174—175°, which is hydrolysed to *piperidino-oxalylhydrazine*, colourless, transparent plates, m. p. 77—79° (*hydrochloride*, m. p. 180°; *benzylidene* derivative, m. p. 201—202°). C. J. S.

Preparation and Hydrolysis of Substituted Cyanamides: Di-*n*-butylcyanamide and Diallylcyanamide. E. B. Vliet (*J. Amer. Chem. Soc.*, 1924, **46**, 1305—1308).—*Di*-n-*butylcyanamide*, a clear, slightly viscous liquid, b. p. 147—151°/35 mm., 187—191°/190 mm., and *diallylcyanamide*, a colourless liquid, b. p. 105—110°/18 mm., 140—145°/90 mm., are obtained by the action of *n*-butyl and allyl bromides, respectively, on a solution of sodium cyanamide obtained by the action of cold sodium hydroxide on an aqueous suspension of commercial calcium cyanamide, the reaction being facilitated by the addition of alcohol. The above cyanamides are hydrolysed to di-*n*-butylamine and diallylamine on boiling with 25% sulphuric acid. F. G. W.

Production of Thiocyanogen by Electrolysis of Alkali Thiocyanates. H. Kerstein and R. Hoffmann (*Ber.*, 1924, **57**, [*B*], 491—496).—Thiocyanogen, first obtained by Söderbäck (A., 1920, i, 219) by the action of bromine on a suspension of silver thiocyanate in carbon disulphide, can be obtained by the electrolysis of alkali thiocyanates in aqueous or alcoholic solutions, using a platinum-gauze anode and a silver cathode. By evaporating the methyl-alcoholic solution at very low pressure, the thiocyanogen was left as a viscous oil which became solid at −70° and gradually crystallised. The thiocyanogen united with thiocyanates to form trithiocyanates, $M(SCN)_3$ (cf. tri-iodides), which behaved precisely like free thiocyanogen except for their smaller sensitiveness towards water. F. A. M.

Reduction of Pyruvylhydroxamic Acid Phenylhydrazone. V. C. Gastaldi (*Gazzetta*, 1924, **54**, 212—213).—Reduction of pyruvylhydroxamic acid phenylhydrazone by means of sodium amalgam at 0° (cf. A., 1923, i, 1236) proceeds in accordance with the scheme: $NHPh{\cdot}N{:}CMe{\cdot}CO{\cdot}NH{\cdot}OH \xrightarrow[-O]{} NHPh{\cdot}N{:}CMe{\cdot}CO{\cdot}NH_2 \xrightarrow[+2H]{} NHPh{\cdot}NH{\cdot}CHMe{\cdot}CO{\cdot}NH_2 \xrightarrow[+H_2O]{} NHPh{\cdot}NH{\cdot}CHMe{\cdot}CO_2H+NH_3$. The intermediate products obtained are thus: (1) α(β-phenylhydrazido)-propionamide, $NHPh{\cdot}NH{\cdot}CHMe{\cdot}CO{\cdot}NH_2$, m. p. 124° (cf. Reissert, A., 1884, 1152; Miller and Plöchl, A., 1892, 1196), and (2) *pyruvamide phenylhydrazone*, $NHPh{\cdot}N{:}CMe{\cdot}CO{\cdot}NH_2$, which crystallises in nacreous, white laminæ, m. p. 144°, and may be obtained also by dehydrogenating compound (1) by treatment with the alkaline tartrate solution used in preparing Fehling's solution. T. H. P.

Derivatives of Pyruvylhydroxamic Acid. VI. C. Gastaldi (*Gazzetta*, 1924, **54**, 214—220).—Pyruvylhydroxamic acid phenylhydrazone and its acetyl derivative, prepared as described by Pickard (T., 1902, **81**, 1573), melt at 178—179° and 142°, respectively, not at 148° and 113°, as stated by this author. Further, the oxime of this acid has m. p. 161° and not 143° as given by Whiteley (T., 1900, **77**, 1046).

Pyruvylhydroxamic acid semicarbazone,

$$NH_2\cdot CO\cdot NH\cdot N\colon CMe\cdot CO\cdot NH\cdot OH,H_2O$$

or $NH_2\cdot CO\cdot NH\cdot N\colon CMe\cdot C(OH)\colon NOH,H_2O$, colourless needles, m. p. 200° (decomp.), gives a deep violet-red coloration with ferric chloride in aqueous solution; its *acetyl* derivative forms colourless prisms, m. p. 170° (decomp.). The *thiosemicarbazone*, $3C_4H_8O_2N_4S,2H_2O$, m. p. 185° (decomp.), forms a silver mirror when heated with ammoniacal silver nitrate. The β-*naphthylhydrazone*, $C_{13}H_{13}O_2N_3$, forms lustrous, orange laminæ or slender needles, m. p. 182° (decomp.), dissolves in concentrated sulphuric acid to a deep yellow solution, and in alcoholic solution gives a dark green coloration with aqueous ferric chloride; its *sodium* salt forms chestnut-red prisms and explodes violently when heated, and its *acetyl* derivative crystallises in orange prisms, m. p. 147—148° (decomp.), and on fusion is converted into 5-*hydroxy*-1-β-*naphthyl*-3-*methyl*-1 : 2 : 4-*triazole*, yellowish-brown prisms, m. p. 199°.

1-β-*Naphthyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*, $C_{14}H_{13}N_3$, obtained when pyruvylhydroxamic acid β-naphthylhydrazone is fused with acetic anhydride, separates in yellow prisms, m. p. 105—106°; its *hydrochloride*, prisms, has m. p. 257°. T. H. P.

Conversion of *n*-Butane-αββ-tricarboxylic Acid into its Triazide and into Aminomethyl Ethyl Ketone. T. Curtius and R. Gund (*J. pr. Chem.*, 1924, [ii], **107**, 177—192).—Ethyl butane-αββ-tricarboxylate (cf. Bischoff, A., 1890, 742), b. p. 153—155°/9 mm., treated with hydrazine hydrate gives the *trihydrazide*, $C_2H_5\cdot C(CO\cdot NH\cdot NH_2)_2\cdot CH_2\cdot CO\cdot NH\cdot NH_2$, needles, m. p. 167°. This is not converted into a hydrazihydrazide by the action of iodine but only into the original acid and hydrazine dihydriodide. The *tribenzylidene* compound, m. p. 244° (decomp.); *derivatives* with salicylaldehyde, m. p. 212°; *p*-tolualdehyde, m. p. 249° (decomp.); *o*-chlorobenzaldehyde, m. p. 262°; *o*-nitrobenzaldehyde, m. p. 303°; acetone, m. p. 156°; and benzophenone, m. p. 162°; the *triacetyl* compound, m. p. 222°; *tribenzoyl* compound, m. p. 236°; *hydrochloride*, m. p. 185°, and *picrate*, m. p. 185°, are described. When treated as hydrochloride with sodium nitrite the trihydrazide is converted into the *triazide*, an explosive lachrymatory oil, decomposing even in ethereal solution at 0°. Treated with aniline in the cold, this gives *butane*-αββ-*tricarboxyanilide*, needles, m. p. 217°; the corresponding *tri*-p-*toluidide* forms prisms, m. p. 186°. With alcohol, the *urethane*, $CEt(NH\cdot CO_2Et)_2\cdot CH_2\cdot NH\cdot CO_2Et$, an oil, is formed, and when this substance is hydrolysed with hydrochloric acid at 80°, the hydrochloride of α-amino-β-ketobutane (Kolshorn, A., 1904, i, 675) is produced. When the triazide is decomposed by heating its solution in benzene the *carbimide*,

$$C_2H_5\cdot C(NCO)_2\cdot CH_2\cdot NCO,$$

is formed. This substance, an oil, interacts with aniline to yield *butenyltri-phenylcarbamide*,

$$CEt(NH\cdot CO\cdot NHPh)_2\cdot CH_2\cdot NH\cdot CO\cdot NHPh,$$

white crystals soon turning yellow, m. p. 225°, which may be hydrolysed giving the above aminoketone, aniline, carbon dioxide, and ammonia. W. A. S.

Rubidium and Cæsium Creatinine Picrates. I. GREENWALD and J. GROSS (*J. Biol. Chem.*, 1924, **59**, 613—614).—The double picrates of creatinine with rubidium and with cæsium, m. p. 256—257° and 255°, respectively, were prepared by mixing hot solutions of creatinine, picric acid, and the sulphate or chloride of the metal. C. R. H.

Ultra-violet Absorption Spectrum of Naphthalene Vapour. V. HENRI and H. DE LÁSZLÓ.—(See ii, 367.)

Methylnaphthalenes. I. α-Methylnaphthalenesulphonic Acids. K. ELBS and B. CHRIST (*J. pr. Chem.*, 1923, [ii], **106**, 17—24). —α-Methylnaphthalene (b. p. 241°, picrate, m. p. 141°) was converted by the action of sulphuric acid at the ordinary temperature into 1-*methylnaphthalene*-4-*sulphonic acid*, which was separated by means of its barium salt, a small amount of an isomeric barium salt being found in the mother-liquors. The free acid is deliquescent, exceedingly soluble in water, and readily soluble in concentrated sulphuric acid. The *barium* salt ($+1H_2O$) crystallises in colourless plates, the *copper* salt ($+4H_2O$) in small, pale green crystals. Attempts to oxidise the methyl group to the carboxyl group by means of potassium permanganate under varying conditions were unsuccessful. The *sulphochloride*, $C_{10}H_6Me\cdot SO_2Cl$, m. p. 81°; *sulphonamide*, m. p. 174°; *sulphonhydrazide*, m. p. 124—125° (decomp.); *acetyl* derivative of the hydrazide, m. p. 220—222° (decomp.); *sulphanilide*, m. p. 158°; the *methyl* ester, m. p. 107°, and the *ethyl* ester, m. p. 98°, are described. 1-*Methylnaphthalene*-4-*sulphinic acid*, obtained by reduction of the sulphochloride with zinc dust, crystallises in needles, m. p. 114—115°; the *sodium* salt ($+3H_2O$) and the *copper* salt are described. 4-*Thiol*-1-*methylnaphthalene*, $C_{10}H_6Me\cdot SH$, results in an impure form on reduction of the sulphochloride with iron turnings and hydrochloric acid; it is a yellow oil distilling between 168° and 178°/25 mm. The *lead* and *mercury mercaptides* form yellow precipitates. 1 : 1′-*Dimethyldinaphthyl* 4 : 4′-*disulphide*, $C_{10}H_6Me\cdot S\cdot S\cdot C_{10}H_6Me$, obtained by the action of alcoholic ammonia on the thionaphthol, is a colourless, crystalline solid, m. p. 114°. 4-Methyl-α-naphthol is obtained from the acid by the ordinary method. F. G. P.

Course of Reaction in the Gattermann Synthesis of Diphenyl and the Formation of Para Chains of Benzene Rings. O. GERNGROSS, L. SCHACHNOW, and R. JONAS (*Ber.*, 1924, **57**, [*B*], 747—750).—In the Gattermann synthesis of diphenyl (A., 1890, 970) a small amount of *p*-phenyldiphenyl is produced simultaneously. The yield of diphenyl diminishes with decrease in alcohol concentration, owing to the diminished solubility of the intermediately formed benzene, which is thus prevented from reacting with fresh diazonium salt. When diphenyldiazonium sulphate was treated with benzene and copper powder in a mixture of acetic, formic, and sulphuric acids, diphenyl (1 g.), *p*-phenyldiphenyl (0·3 g.) and *pp'*-diphenyldiphenyl (0·02 g.), were obtained. The mechanism of the reaction is therefore $C_6H_4Ph{\cdot}N_2Cl+C_6H_6=Ph{\cdot}C_6H_4{\cdot}Ph+N_2+HCl$. By a modification of the usual Gattermann synthesis from aniline (31 g.), diphenyl (4·2 g.), *p*-phenyldiphenyl (1·8 g.), *pp'*-diphenyldiphenyl (1·0 g.), and didiphenylylbenzene (0·11 g.) were isolated. (Cf. also *infra.*) F. A. M.

Studies in the Anthracene Series. IX. E. de B. Barnett and J. W. Cook (*J. Chem. Soc.*, 1924, **125**, 1084—1087).—The reaction between anthracene and bromine is reversible (cf. T., 1923, **123**, 1994), and by treatment of the anthracene dibromide with dilute hydriodic acid or compounds such as phenol which readily take up bromine, anthracene is regenerated. By the decomposition of anthracene dibromide on warming, dibromoanthracene is formed in addition to 9-bromoanthracene, but the formation of the dibromo compound is inhibited by phenol. The action of chlorine on 9-bromoanthracene is more rapid than on anthracene, but the only product isolated was 9-*chloro*-10-*bromoanthracene*, lemon-yellow needles, m. p. 207°. The same product was obtained by the action of sulphuryl chloride. On treatment with nitric acid in glacial acetic acid, 9-bromoanthracene yields 9 : 10-dibromoanthracene, 9-nitroanthrone, and probably a little bromonitroanthracene. The mechanism of the reaction is discussed. R. B.

Reduction of Organic Halogen Compounds. VII. 3-Phenyl-1-diphenylmethylene-indene. K. Brand and L. W. Berlin (*Ber.*, 1924, **57**, [*B*], 846—847; cf. A., 1921, i, 783).—The constitution of the hydrocarbon, m. p. 207—208°, obtained from βγ-dichloro-ααδδ-tetraphenyl-Δ^{β}-butene has now been proved by its synthesis from 3-phenylindene and benzophenone in presence of sodium ethoxide, and the formula previously ascribed,

$C_6H_4{<}{\begin{matrix}\text{——CPh}\\ \text{C(:CPh}_2\text{)}\end{matrix}}{>}CH$, is therefore correct. The synthesis also confirms the structure assigned to the substance $C_{32}H_{28}O_4$, m. p. 173° (A., 1921, i, 787), obtained by the reduction of βγ-dichloro-ααδδ-tetra-*p*-anisyl-Δ^{β}-butene, and proves that compounds of the tetra-arylbutane series are easily converted into indene derivatives. R. B.

A Para Linking of the Benzene Ring; Extension of the Gattermann Diphenyl Synthesis and Quinquephenyl [Didiphenylylbenzene], a Straight Chain of Five Benzene Nuclei. [illegible] Gross and M. Dunkel (*Ber.*, 1924, **57**, [*B*], 739—746).—[illegible] diazotised in a mixture of concentrated sulphuric acid [illegible] acid, by amyl nitrite; glacial formic acid was [illegible] powder by degrees at 0—2°. On steam distillation diphenyl was obtained in the distillate (10·3%); 24·8% of the non-volatile, insoluble residue sublimed in a vacuum, at 135° to 400°/30 mm. This product was separated into *p*-phenyldiphenyl, *pp'*-diphenyldiphenyl, and didiphenylylbenzene,

$$C_6H_4Ph\cdot C_6H_4\cdot C_6H_4Ph.$$

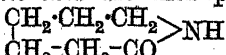
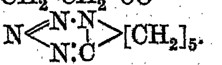
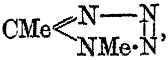
The *p*-phenyldiphenyl had m. p. 209·5°, as compared with 207·5° when made from benzenediazonium chloride diphenyl, and aluminium chloride, and its other properties differ slightly from those given in the literature. The *pp'*-diphenyldiphenyl had m. p. 320°, in agreement with Ullmann's figure (A., 1904, i, 725). *Didiphenylylbenzene* is a faintly yellow substance, m. p. 388·5°, very sparingly soluble in all organic solvents; it was also prepared by Pummerer's method (A., 1922, i, 24, 1196) from *p*-iodophenyldiphenyl, *p*-iododiphenyl, and silver powder. F. A. M.

Specific Heats of certain Organic Liquids at Elevated Temperatures. J. W. Williams and F. Daniels.—(See ii, 450.)

Equilibrium of the System Ferric Chloride–Aniline Hydrochloride–Hydrogen Chloride–Water at 25°. Y. Osaka, G. Shima, and R. Yoshida (*Mem. Coll. Sci. Kyōtō*, 1924, 7, 69—76).—Investigation of this system from the point of view of the phase theory indicates the existence of the two double salts:

$$FeCl_3,6(NH_2Ph,HCl),$$

in yellowish crystals, and $FeCl_3,2(NH_2Ph,HCl)$ in bluish-green, acicular crystals. The two hydrated salts obtained by McKenzie (A., 1913, i, 1321) were not formed under the conditions employed. T. H. P.

The Imino Residue. K. F. Schmidt (*Ber.*, 1924, 57, [*B*], 704—706).—Azoimide is converted by concentrated sulphuric acid partly into hydroxylamine, some oxidation also occurring. At the atmospheric temperature, azoimide dissolved in benzene is transformed by concentrated sulphuric acid mainly into hydrazine, hydroxylamine and aniline being produced in small amount; at 60°, the main product is aniline sulphate, very little hydrazine being formed. Addition of carbonyl derivatives greatly accelerates the decomposition of azoimide by concentrated sulphuric acid and causes the immediate withdrawal of the liberated radical, NH, from the oxidising action of the acid, so that it is possible to convert N_3H quantitatively into NH. Ketones yield acid amides, $R\cdot CO\cdot R + NH \longrightarrow R\cdot CO\cdot NHR$, whereas aldehydes give nitriles or substituted formamides. α-Ketonic acids are converted into α-amino acids, the yields being 80—98% of the theoretical (glycine, α-aminobutyric acid, leucine, *α-amino-δ-methylhexoic acid*, phenylalanine, aspartic acid, and *α-aminodibenzylacetic acid* are thus prepared). *cyclo*Hexanone gives ε-leucyl-lactam,  $\begin{array}{l}CH_2\cdot CH_2\cdot CH_2\\ CH_2-CH_2-CO\end{array}>NH$, or with an excess of azoimide the tetrazole,  $N<\begin{array}{c}N\cdot N\\ N:C\end{array}>[CH_2]_5$. Acyclic ketones likewise yield tetrazoles with an excess of azoimide, acetone giving the compound  $CMe<\begin{matrix}N{-}{-}N\\ NMe{\cdot}N\end{matrix}$, whereas benzophenone gives 5-anilino-1-phenyl-1 : 2-dihydrotetrazole. H. W.

Nitrogen Chlorides derived from Nitro-substituted Acetanilides. F. D. Chattaway and H. J. Dowden (*J. Chem. Soc.*, 1924, **125**, 1195—1197).—*N*-Chloro derivatives of polynitroacetanilides are not transformed into chloronitroacetanilides, but are hydrolysed and decomposed, or the original nitroacetanilide is regenerated. The transformation of *N*-chloro-2- and -3-nitroacet-*p*-toluidides is also inhibited by the presence of the nitro group. N-*Chloro*-2 : 4-*dinitroacetanilide*, m. p. 54—55°, is obtained by the action of chlorine on 2 : 4-dinitroacetanilide in acetic acid solution. 6-Chloro-2 : 4-dinitroacetanilide, m. p. 221°, on treatment with hypochlorous acid in chloroform yields N : 6-*dichloro*-2 : 4-*dinitroacetanilide*, m. p. 68·5°. 2 : 4 : 6-Trinitroacetanilide is not attacked by chlorine in acetic acid solution, but in sodium hydroxide solution it yields N-*chloro*-2 : 4 : 6-*trinitroacetanilide*, m. p. 127·5°. N-*Chloro*-2-*nitroacet*-p-*toluidide*, m. p. 125—126°, is obtained by the action of hypochlorous acid on 2-nitroacet-*p*-toluidide in chloroform. N-*Chloro*-3-*nitroacet*-p-*toluidide*, m. p. 51·5°, is similarly prepared from the 3-nitrotoluidide. R. B.

Preparation of Anilides of Glycine. P. Karrer and W. T. Haebler (*Helv. Chim. Acta*, 1924, **7**, 534—536).—Glycineanilide is simply prepared by reducing Sandmeyer's oximinoacetanilide (A., 1919, i, 318) either electrolytically or with zinc dust and acetic acid. *Glycylanthranilic acid*, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH_2$, obtained by reduction of oximinoacetylanthranilic acid, has m. p. 233—234°; *sulphate*, white crystals. Glycyl-*p*-phenetidine (phenocoll) is obtained similarly from oximinoacetyl-*p*-phenetidine. E. H. R.

Naphthol AS [2-Hydroxy-3-naphthoanilide] Derivatives. M. Battegay, C. Langjahr, and P. Rettig (*Chim. et Ind.*, 1924, **11**, 453—455).—β-*Naphthaquinone*-1-*oxime*-3-*carboxyanilide*, obtained by the action of nitrous acid on Naphthol AS, forms red needles which decompose at 200° without melting, soluble in warm sodium hydroxide solution. The sodium compound, when treated with sodium hydrogen sulphite solution, yields a hydrogen sulphite compound which dyes cotton better than does the corresponding β-naphthol derivative. 1-*Amino*-2-*hydroxynaphthalene*-3-*carboxyanilide*, obtained by the reduction of the quinoneoxime, crystallises in fine needles, m. p. 180°. β-*Naphthaquinone*-3-*carboxyanilide*, brick-red crystals, m. p. 204°, yields a red solution in sulphuric acid. The *Meldola-blue*, prepared from Naphthol AS instead of β-naphthol, is insoluble in water but soluble in acetic acid; it dyes [illegible] duller shade than does ordinary Meldola-blue. W. P. S.

Reactions of Tetryl [2 : 4 : 6-Trinitrophenylmethylnitro- [illegible] Davis and C. F. H. Allen (*J. Amer. Chem. Soc.*, [illegible]).—Commercial samples of tetryl often con- [illegible] tetryl is heated with hexyl or *n*-butyl alcohol, methylpicramide (picrylmethylamine) is formed in small quantities (cf. Mertens, A., 1886, 1022). Tetryl is not affected by prolonged boiling with dilute sulphuric acid, but with aqueous chromic acid it yields picric acid. In the presence of glacial acetic acid, tetryl is destroyed by chromic acid. It is rapidly dissolved by concentrated sulphuric acid at 100°, forming a red solution, and is reprecipitated on pouring this solution on to ice. If the solution is allowed to stand for some days and then poured on to ice, a gummy material is precipitated which dissolves in warm alcohol. The solution deposits 20% of the theoretical yield of picrylmethylamine. As picrylmethylamine yields tetryl on nitration, the reaction is reversible. [Cf. *B.*, 1924, 539.] A. C.

Colour Tests for Nitro Derivatives of Diphenylamine. T. L. DAVIS and A. A. ASHDOWN (*J. Amer. Chem. Soc.*, 1924, **46**, 1051—1054).—Such nitro derivatives as were likely to be found in smokeless powder which has been stored for some time, were prepared in a state of high purity (detailed methods are given), and their colour reactions with alcoholic solutions of sodium hydroxide, ammonia, and sodium cyanide, as well as with sulphuric acid, were examined under standardised conditions. The derivatives examined were *o*-, *m*-, and *p*-nitrodiphenylamine; 2 : 4-, 2 : 4′-, 4 : 4′-dinitro-; 2 : 4 : 6- and 2 : 4 : 4′-trinitro-; 2 : 4 : 2′ : 4′- and 2 : 4 : 6 : 4′-tetranitro-diphenylamines, together with diphenylnitrosoamine. The colours are compared according to the standard colour chart of Mulliken ("Identification of Pure Organic Compounds," Vol. I). An attempt to prepare *o*- and *p*-nitrodiphenylnitrosoamines by nitrating diphenylnitrosoamine in glacial acetic acid at 15° led to the formation of *p*-nitrosodiphenylamine (Fischer-Hepp rearrangement) and nitrodiphenylamines with nitro groups in the para-position. Derivatives with melting points higher than previously recorded were: 4 : 4′-dinitro-, 216—216·5°; 2 : 4′-dinitro-, 220—221·5°; and 2 : 4 : 2′ : 4′-tetranitro-diphenylamine, 201—201·5°. A. C.

Hydrindene. II. W. BORSCHE and G. JOHN (*Ber.*, 1924, **57**, [*B*], 656—662; cf. Borsche and Pommer, A., 1921, i, 168).—5-Aminohydrindene, coarse needles, m. p. 37—38°, b. p. 247—249°/745 mm., is prepared by the action of phosphorus pentachloride on an ethereal solution of 5-acetylhydrindeneoxime or of bromine and sodium hydroxide solution on hydrindene-5-carboxyamide. When diazotised and coupled with β-naphthol or 5-hydroxyhydrindene, it yields *5′-hydrindeneazo-β-naphthol*, carmine-red leaflets, m. p. 156—157°, or *5′-hydrindene-4(?)-azo-5-hydroxyhydrindene*, brown needles, decomp. 175°.

5-Hydroxyhydrindene, m. p. 55°, is obtained in moderate yield from 5-aminohydrindene through the diazo compound, or more readily by fusing sodium hydrindene-5-sulphonate with sodium hydroxide at 280—290°; the corresponding *benzoate* forms colourless leaflets, m. p. 106—107°. The phenol couples with diazobenzene-*p*-sulphonic acid to give the orange-red *dye*,

$C_{15}H_{12}O_4N_2SNa_2$,

which is converted by sodium hyposulphite into 4(?)-amino-5-hydroxyhydrindene, m. p. 183—184°. 4 : 6-*Dinitro-5-hydroxyhydrindene* forms dark yellow leaflets or needles, m. p. 106—107°. 5-Hydroxyhydrindene is converted by bromine in glacial acetic acid solution into a colourless, crystalline substance, m. p. 40—41°, which loses hydrogen bromide when kept and passes into dibromo-5-hydroxyhydrindene, a colourless liquid (*benzoate*, leaflets, m. p. 139°).

5 : 5′-*Dihydrindyl ketone*, $C_{19}H_{18}O$, m. p. 117—118°, b. p. 245—250°/15 mm., is prepared from hydrindene-5-carboxylic chloride and hydrindene in the presence of carbon disulphide and aluminium chloride; the corresponding *oxime*, colourless needles, m. p. 173°, is isomerised to *hydrindene-5-carboxy-5′-hydrindylamide*, colourless needles, m. p. 173°, which is also obtained from hydrindene-5-carboxylic chloride and 5-aminohydrindene in the presence of pyridine. 5-Acetylhydrindene is converted successively into 4-*nitro-5-acetylhydrindene*, long, colourless needles, m. p. 51—52°, and 4-*nitro-5-acetylhydrindeneoxime*, colourless needles, m. p. 153—154°. The latter substance is transformed by successive treatment with phosphorus pentachloride and boiling hydrochloric acid (20%) into 4-*nitro-5-aminohydrindene*, orange-red needles, m. p. 92—93°. 4-*Nitro-5-benzoylaminohydrindene*, yellow crystals, m. p. 118—119°, is reduced by tin and fuming hydrochloric acid to 2-*phenyl*-4 : 5-*trimethylenebenzíminazole*,

$$CH_2{<}{}^{CH_2}_{CH_2}{>}C_6H_2{<}{}^{—N}_{NH}{>}CPh,$$

b. p. about 280°/50 mm., m. p. 224—226° (decomp.). De-amination of 4-nitro-5-aminohydrindene in the usual manner gives 4-*nitrohydrindene*, a yellow liquid, which is reduced by iron and acetic acid to 4-*aminohydrindene*, a colourless liquid, b. p. 235°/754 mm. (*benzoyl* derivative, colourless leaflets, m. p. 135—136°; *azo* dye, obtained with β-naphthol, long, red needles, m. p. 141—142°). The base is also obtained by converting hydrindene-5-carboxylic acid into *nitrohydrindene-5-carboxylic acid*, m. p. about 140° (*amide*, colourless leaflets, decomp. 194°), reduction of the acid with tin and hydrochloric acid, and distillation of the crude amino-acid with potassium hydroxide. H. W.

Condensation of Cyclic Hexenes with Phenol. (Chemical Structure of Lignin.) W. Schrauth and K. Quasebarth (*Ber.*, 1924, 57, [*B*], 854—858).—By condensing phenol with *cyclo*hexene in the presence of sulphuric and acetic acids (cf. Koenigs, A., 1891, i, 208, 571) *p-cyclo*hexylphenol, m. p. 130°, identical with that previously prepared from phenol and *cyclo*hexanol (A., 1923, i, 1084) is obtained. Condensation in the presence of concentrated hydrochloric acid gives the same product in poorer yield, with some [illegible] *cyclohexyl ether*, b. p. 125—127°/10 mm. In the absence of catalyst no condensation takes place. Similar results were [illegible] the methyl*cyclo*hexenes. Condensation of phenol [illegible] *cyclo*hexenes prepared from 3-methyl-, 4-methyl-, [illegible] *cyclo*hexan-1-ol by Koenigs' method yielded [illegible] *hexylphenol*, felted needles, m. p. 112·5°, whilst condensation with hydrochloric acid gave the same product in poorer yield, together with phenyl methyl*cyclo*hexyl ether, b. p. 129—130°/8·5 mm., d_4^{20} 0·9857. 1 : 3-Dimethyl-Δ^5-*cyclo*hexene and phenol in the presence of hydrochloric acid yielded *dimethyl*cyclo*hexylphenol*, fine needles, m. p. 68—73°, which gives the Liebermann reaction; octahydronaphthalene similarly yields *decahydronaphthylphenol*, fine needles, m. p. 127—128°. The alkali salts of these two phenols possess lathering properties. Similar products were obtained from pinene and limonene by condensation in the presence of hydrochloric acid, but the products could not be satisfactorily purified. All the condensation products are readily soluble in organic solvents.

The property of reacting in this way with phenol appears to be characteristic of the tetrahydrobenzene ring carrying side-chains or other ring systems, and in conjunction with the observation that lignin dissolves in phenol in the presence of traces of mineral acid, supports the view that lignin possesses an unsaturated hydroaromatic structure (cf. A., 1923, i, 443; ii, 502). R. B.

***cyclo*Hexyl Ether.** W. SCHRAUTH and W. WEGE (*Ber.*, 1924, 57, [*B*], 858).—Phenyl *cyclo*hexyl ether (cf. preceding abstract) in the presence of active nickel at 165—170° and under 10—15 atm., is readily converted into *cyclo*hexyl ether, $(C_6H_{11})_2O$, a mobile, colourless liquid, b. p. 239—240°, d_4^{20} 0·9241, identical with the product described by Willstätter and Hatt (A., 1912, i, 544). The discrepancy in the results obtained by Ipatiev (A., 1908, i, 342) is attributed to the high temperature and pressure employed by him (cf. A., 1923, i, 204). R. B.

Action of Chloropicrin on Phenol. S. BERLINGOZZI and P. BADOLATO (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 290—292).—The interaction of chloropicrin and phenol in presence of potassium hydroxide results in elimination of the nitro group, which effects oxidation and is itself reduced to ammonia. The principal products are *o*- and *p*-hydroxybenzaldehydes and the corresponding acids, and considerable quantities of pararosolic acid are formed, probably by condensation of the phenol with the hydroxybenzaldehyde.
T. H. P.

Tautomerism with Respect to Nitrosophenols. H. H. HODGSON (*J. Soc. Dyers and Col.*, 1924, **40**, 167—174).—No conclusion can be drawn from the work of previous investigators (cf. Bridge, A., 1894, i, 25) as to the existence of nitrosophenols as such, since the conditions employed in preparing derivatives all favour conversion into the quinone-oxime form before or during reaction. Similar causes are responsible for the poor yield and impure product obtained in nitrosating phenol in the usual way. If the nitrosation be carried out by dissolving the phenol in dilute sodium hydroxide solution, adding an excess of sodium nitrite, and then running dilute sulphuric acid in gradually, a clean product of m. p. 133° is obtained. When *m*-chlorophenol is nitrosated in this way it gives 60% of the theoretical yield of m-*chloro*-p-*nitrosophenol*, needles, m. p. 135·8°, affording *m*-chloro-*p*-nitrophenol on oxidation. When boiled with dilute hydrochloric acid, the nitroso compound is converted into syn(?)-2-*chlorobenzoquinonemonoxime*, orange crystals, m. p. 172° (decomp.), and this is further converted into the *anti*(?) form, yellow needles, m. p. 178°, by solution in dilute sodium hydroxide and reprecipitation. A mixture of the two substances melts at 170·6°. The reverse change is brought about by treatment with hot dilute acid. Anti(?)-2-*chlorobenzoquinonemonoxime* may also be obtained directly from the true nitrosophenol by dissolving the latter in a saturated solution of sodium carbonate and reprecipitating it with acid. Alkali hydroxide causes further changes, impure products being obtained. W. A. S.

Reactions of Strongly Electropositive Metals with Organic Substances in Liquid Ammonia Solution. V. Syntheses of Oxygen and Sulphur Ethers and of Alkyl Derivatives of Ammono Acids. G. F. WHITE, A. B. MORRISON, and E. G. E. ANDERSON (*J. Amer. Chem. Soc.*, 1924, 46, 961—968).—A number of organic compounds, containing hydroxyl, thiol, amino, or imino groups, which possess acidic character, react with the alkali metals or with alkali amides in liquid ammonia. The salts formed are more or less soluble in the liquid ammonia, and many of them react in that medium with organic halides and form compounds in which the hydrocarbon radical of the halide has replaced the metal atom of the salt. The latter reaction is often quantitative, particularly in cases where there is no action between the halide and liquid ammonia. The speed of the reaction depends largely on the solubility of the salt formed. The reactions approach the ionic type, being completed within 5 minutes at −33°. Methyl iodide reacts vigorously with liquid ammonia, producing tetramethylammonium iodide, and is therefore not suitable for these reactions. Ethyl iodide and benzyl chloride have only a slight action, whilst *n*-butyl bromide, ethylene bromide, and iodobenzene do not react at all. Aliphatic ethers were synthesised by dissolving an atomic proportion of potassium (or sodium) in liquid ammonia, adding a molecular proportion of an alcohol (when the alkoxide was partly or wholly precipitated) followed by the halide. The ether was isolated after distilling off the ammonia under water. Its yield depended largely on the solubility of the alkoxide. The yield of ethyl ether was 71% of theory, ethyl *n*-butyl ether 19%, benzyl ethyl ether 81%, benzyl ether 55%. The phenoxides of the alkali metals are more soluble in liquid ammonia and react readily with alkyl halides. Anisole was obtained in 42% yield by passing gaseous methyl chloride into a solution of sodium phenoxide in liquid ammonia. Phenetole was obtained in 59·5% yield, using ethyl bromide. A small amount of phenetole is obtained when ethyl iodide is allowed to stand with phenol in liquid ammonia in the absence of a metal. Phenyl *n*-butyl ether was obtained in 28% yield. Neither ethylene bromide nor chloride reacts with sodium phenoxide to form diphenyl ethylene ether. α-Naphthol reacts with sodium in liquid ammonia, giving a clear solution, but no hydrogen is given off, the naphthol being partly reduced to tetrahydronaphthol. A mixture of the ethers of naphthol and tetrahydronaphthol was obtained on adding an alkyl halide. β-Naphthyl ethyl ether was obtained in this way using ethyl iodide; yield 61% of theory. Resorcinol and ethyl iodide gave small yields of the mono- and di-ethyl ethers. Thiophenols are more reactive, and evidence of the formation of an ammonium phenyl sulphide was obtained. Thiophenol added to ethyl bromide in liquid ammonia resulted in 76% of the theoretical yield of the thio-ether, the preparation of a metal compound being unnecessary. Phenyl *n*-propyl sulphide and diphenyl ethylene disulphide were prepared in 86 and 98% yields, respectively. Certain amino and imino compounds of acidic character form metallic amides which react with alkyl (not aryl) halides. Thus acetamide forms potassium acetamide which reacts with ethyl bromide to form acetethylamide (34% yield). Diphenylamine gives a soluble potassium compound which with ethyl bromide leads to a quantitative yield of diphenylethylamine. Acetethylanilide (40% yield) and ethylphthalimide (small yield) were similarly prepared. A. C.

***o*-Nitrotoluene-*p*-sulphon-*p*-anisidide and its Nitration Products.** F. Reverdin (*Helv. Chim. Acta*, 1924, **7**, 567—574).—The following nitro derivatives of *o*-nitrotoluene-*p*-sulphon-*p*-anisidide were prepared to investigate the formation by such compounds of molecular compounds and substitution products with aliphatic and aromatic amines. Nitration of *o*-nitrotoluene-*p*-sulphon-*p*-anisidide in acetic acid solution with nitric acid, *d* 1·38, at about 0° gives a high yield of o-*nitrotoluene*-p-*sulphon*-3-*nitro*-p-*anisidide*, lemon-yellow crystals, m. p. 135°. It gave no definite compounds with amines. Nitration of a paste of the anisidide with glacial acetic acid at 0°, using nitric acid *d* 1·51, gave as principal product o-*nitrotoluene*-p-*sulphon*-2 : 3-*dinitro*-p-*anisidide*, pale yellow, transparent prisms, m. p. 178—179°. This forms a *compound*, m. p. 158°, with ethylamine, and a particularly stable *compound* with diethylamine, $C_{14}H_{12}O_9N_4S,NHEt_2$, lemon-yellow needles, m. p. 194°. As a by-product of the second method of nitration there is formed o-*nitrotoluene*-p-*sulphon*-2 : 5-*dinitro*-p-*anisidide*, lemon-yellow needles, m. p. 152°. By further nitrating the above 3-nitro-*p*-anisidide, o-*nitrotoluene*-p-*sulphon*-3 : 5-*dinitro*-p-*anisidide* was obtained, pale yellow needles, m. p. 147°. By heating 2 : 3-dinitro-*p*-anisidide with nitric acid, *d* 1·4, at 70—80°, o-*nitrotoluene*-p-*sulphon*-2 : 3 : 5-*trinitro*-p-*anisidide* is formed, small, white prisms, m. p. 188—189°. This forms *compounds* with ethylamine, $C_{14}H_{11}O_{11}N_5S,NH_2Et$, orange prisms, m. p. indistinct, near 149°, and with diethylamine, $C_{14}H_{11}O_{11}N_5S,NHEt_2$, lemon-yellow prisms, m. p. about 168—169°. With aniline it forms a substitution *compound*, $C_{20}H_{17}O_9N_5S$, yellow needles, m. p. 210°. The 2 : 3-*dinitro*-p-*anisidide* also forms a substitution *compound* with aniline, $C_{20}H_{18}O_7N_4S$, red needles, m. p. 175—176°. E. H. R.

Sulphur Phenyl Chloride [Chlorothiolbenzene]. H. LECHER and F. HOLSCHNEIDER (*Ber.*, 1924, 57, [*B*], 755—758; cf. Zincke and Baeumer, A., 1918, i, 537).—The simplest member of the series of sulphur aryl chlorides discovered by Zincke (cf. A., 1912, i, 763) has been obtained by converting phenylthiol thiocyanate (A., 1922, i, 641) with diethylamine in ethereal solution into *diethylaminothiolbenzene* (*benzenesulphendiethylamide*), $SPh{\cdot}NEt_2$, colourless fluid, b. p. 90°/3·5 mm., which on treatment with hydrogen chloride in absolute ether yields *chlorothiolbenzene*, PhSCl, a red, fuming liquid, b. p. 73—75°/9 mm. Chlorothiolbenzene can also be obtained by the action of chlorine on thiophenol or diphenyl disulphide in carbon tetrachloride solution. Chlorothiolbenzene closely resembles sulphur dichloride both in odour and in absorption spectrum. Its constitution follows from its reaction with diethylamine to give diethylaminothiolbenzene, with zinc dust giving diphenyl disulphide, and with β-thionaphthol yielding phenyl β-naphthyl disulphide. R. B.

Interconversion of some Isomeric Cyclic *cis*- and *trans*-1 : 2-Glycols. P. H. HERMANS (*Ber.*, 1924, 57, [*B*], 824—827).—During the investigation of the equilibrium proportions of the *cis*- and *trans*-isomerides of certain glycols, viz., hydrindene-1 : 2-diol, tetrahydronaphthalene-1 : 2-diol and -2 : 3-diol, by the acetone method (cf. A., 1921, i, 663), it was found that equilibrium constants could not be obtained, the *cis*-diol obtained by hydrolysing the acetone compound with boiling dilute acid being partly converted into, and therefore contaminated with, the *trans*-isomeride. The reverse transformation occurs on boiling the pure *trans*-diol with dilute acid, and in boiling dilute acid solution the three 1 : 2-glycols named give equilibrium mixtures of the *cis*- and *trans*-forms. The pure *cis*-isomerides are obtained when the hydrolysis of the acetone compound is carried out with 1·5% sulphuric acid in aqueous acetone below 50°. From the fact that isomerisation does not occur during the formation or hydrolysis of the acetone compound, it is deduced that in these reactions only the O—H linkings of the glycol are concerned and not the C—O linkings, an observation which has some significance for the mechanism of the mutarotation of sugars. The isomerisation was not observed in the case of *cyclo*hexane-1 : 2-diol. R. B.

Derivatives of *iso*-α-Naphthyl-1 : 4-dihydroxy-β-naphthylsulphone. II. O. HINSBERG (*Ber.*, 1924, 57, [*B*], 838—840; cf. A., 1919, i, 202).—By crystallising α-naphthyl-1 : 4-dihydroxy-β-naphthylsulphone twice from acetic acid the yield of *iso*-α-naphthyl-2-α-naphthaquinonylsulphoxide is considerably improved and the by-product melting at 225° is not formed. The sulphoxide is also formed when the dihydroxysulphone is boiled in acetic acid solution for 6 hours. By reduction with zinc dust and sodium hydroxide in the presence of ammonia, the sulphoxide yields a grey substance, changing to bright yellow crystals, m. p. 110°. Reduction of the *iso*-α-naphthyl-2-α-naphthaquinonylsulphone (obtained by oxidation of the sulphoxide, A., 1919, i, 202), with sulphurous acid and hydriodic acid in acetic acid solution, regenerates the *iso*sulphoxide. The sulphoxide and sulphone are distinguished by their behaviour with ammoniacal methyl alcohol. The sulphone dissolves readily and the solution remains clear on dilution, whilst the sulphoxide only partly dissolves on boiling, and the bright yellow solution becomes turbid on adding water. Sodium hydroxide converts the sulphone into a *substance*, $C_{20}H_{11}O_5SNa_2,0{\cdot}5H_2O$, bright yellow needles, probably the sodium salt of *iso*-α-naphthyl-2-α-hydroxynaphthaquinonylsulphone, $C_{10}H_7{\cdot}SO_2{\cdot}C_{10}H_4O_2(OH)$. Compounds of the *iso*-series crystallise from chloroform with 0·5 mol. of solvent. R. B.

Configuration of the Hydrobenzoins in Connexion with the Situation of the Hydroxyl Groups in Space. J. Böeseken and P. H. Hermans (*Proc. K. Akad. Wetensch.*, 1924, **27**, 178—183).—Substitution of hydrogen atoms attached to the α-carbon atom of α-hydroxy acids by alkyl or phenyl groups renders the two hydroxyl groups more readily accessible to boric acid. That this substitution also favours the formation of cyclic acetone compounds is indicated by Willstätter and Königsberger's observations (A., 1923, i, 1172).

The effects of inactive and racemic hydrobenzoins on the conductivity of boric acid are analogous to those produced by esters of tartaric acid, from which it is concluded that the mutual repulsion of the phenyl groups exceeds that of the hydroxyl groups, and the hydroxyl groups in racemic hydrobenzoin are consequently strongly inclined towards each other. These results are discussed in their relationship to those previously obtained. T. H. P.

Semipinacolinic Transformation of Arylhydrobenzoins. Comparative Migratory Tendencies of Naphthyl and Phenyl Radicals. A. Orékhoff and M. Tiffeneau (*Compt. rend.*, 1924, **178**, 1619—1621).—In the pinacolinic transposition, the naphthyl radical, like all substituted phenyl radicals, tends to migrate more readily than the phenyl group itself. To ascertain if this is the case also in the semipinacolinic conversion, the authors have investigated the two reactions: (I) $C_{10}H_7{\cdot}CPh(OH){\cdot}CHRI \xrightarrow[-HI]{+AgNO_3} C_{10}H_7{\cdot}CPh(O{\cdot}){\cdot}CHR{\cdot}$, and (II) $C_{10}H_7{\cdot}CPh(OH){\cdot}CHR{\cdot}OH \xrightarrow[-H_2O]{H_2SO_4} C_{10}H_7{\cdot}CPh(O{\cdot}){\cdot}CHR{\cdot}$.

Reaction (I) yielded no useful result since, in each of the instances examined, the action of silver nitrate causes loss, not of HI, but of HOI, the hydrocarbon used for preparing the iodohydrin being regenerated. As regards reaction (II), concentrated sulphuric acid converts αβ-dihydroxy-αβ-diphenyl-β(α-naphthyl)ethane into α-naphthyldeoxybenzoin, m. p. 108—109°. This ketone was obtained by McKenzie and Roger (T., 1924, **125**, 845), who did not, however, fix its constitution; the latter is evident from the fact that it yields benzoic acid and phenyl-α-naphthylmethane when treated with alcoholic potassium hydroxide. Evidently the action of the sulphuric acid results in elimination of the secondary hydroxyl group and in semipinacolinic transposition:

$$C_{10}H_7\cdot CPh(OH)\cdot CHPh(OH)-H_2O \longrightarrow COPh\cdot CHPh\cdot C_{10}H_7.$$

That the reaction takes place in this manner is rendered more probable by the fact that McKenzie and Richardson (T., 1923, **123**, 79) obtained the same ketone by the action of nitrous acid on the amino-alcohol corresponding with αβ-dihydroxy-αβ-diphenyl-β(α-naphthyl)ethane, by so-called "semipinacolinic de-amination."

T. H. P.

Insecticides. VII. Syntheses of Chrysanthemumic Acid and other *cyclo*Propanecarboxylic Acids with Unsaturated Side Chains. H. Staudinger, O. Muntwyler, L. Ruzicka, and S. Seibt (*Helv. Chim. Acta*, 1924, **7**, 390—406).—The monocarboxylic acid obtained from pyrethrine I, one of the active constituents of insect powder (this vol., i, 510), and identified as 2 : 2-dimethyl-3-*iso*butenyl*cyclo*propane-1-carboxylic acid, has been synthesised by condensing βε-dimethyl-$\Delta^{\beta\delta}$-hexadiene with ethyl diazoacetate. (The hexadiene was obtained in a novel manner by distilling βε-dichloro-βε-dimethylhexane with soda-lime.) A mixture of *cis*- and *trans*-acids was thus obtained, forming a colourless oil, b. p. 140—145°/12 mm., from which on cooling the *cis*-isomeride gradually separated, m. p. 115—116°. The *trans*-isomeride was only obtained in an impure form, b. p. 145—146°/13 mm. By the action of ozone, the two isomerides give, respectively, *cis*- and *trans*-caronic acid. Both acids give insecticidal esters with pyrethrolone, that from the *trans*-acid being the more active. The natural ester is from the d-*trans*-acid, but the synthetic acid has not yet been resolved. A number of related acids were also synthesised, using other butadiene derivatives, but only those from βγ-dimethylbutadiene and isoprene gave insecticidal esters with pyrethrolone, and these were weaker than the true pyrethrines. Purely aliphatic acids of similar structure but without the *cyclo*propane ring, such as βζ-dimethyl-Δ^{ϵ}-heptene-γ-carboxylic acid, $CHMe_2\cdot CH(CO_2H)\cdot CH_2\cdot CH{:}CMe_2$, do not form insecticidal esters.

By the action of ethyl diazoacetate on βδ-dimethyl-$\Delta^{\beta\delta}$-hexadiene an ester was obtained which on hydrolysis gave an *acid*, $C_{10}H_{16}O_2$, b. p. 140—145°/13 mm., which appeared to be a mixture of isomerides. Using β-methyl-$\Delta^{\beta\delta}$-hexadiene and βδ-dimethyl-$\Delta^{\alpha\gamma}$-pentadiene, mixed products were also obtained. From ethyl diazoacetate and βγ-dimethylbutadiene, 2-*methyl*-2-iso*propenyl*cyclo*propanecarboxylic acid*, b. p. 122—123°/15 mm., was obtained; *chloride*, b. p. 90°/11 mm. By oxidation with ozone followed by permanganate, the acid gave a *methyl*cyclo*propanedicarboxylic acid*, m. p. 168—169°. Ethyl diazoacetate and $\Delta^{\beta\delta}$-hexadiene give 2-*methyl*-3-*propenyl*cyclo*propanecarboxylic acid*, a liquid, b. p. 126°/9 mm.; *chloride*, b. p. 86°/9 mm. Isoprene and ethyl diazoacetate give trans-2-iso*propenyl*cyclo*propanecarboxylic acid*, a colourless oil, b. p. 115—119°/12 mm.; *chloride*, b. p. 62—64°/13 mm. From its ozonide was obtained 2-*acetyl*cyclo*propanecarboxylic acid*, crystals, m. p. 52—54° (*semicarbazone*, m. p. 177—179°). Further oxidation with permanganate gives *trans-cyclo*propane-1 : 2-dicarboxylic acid. Hydrocarbons of the terpene series also condense with ethyl diazoacetate to give *cyclo*propanecarboxylic acid derivatives of uncertain constitution.

By condensing ethyl methylmalonate with dimethylallyl bromide, *αδ-dimethyl-*Δ^{γ}*-hexenoic acid* was obtained, b. p. 125°/15 mm.; *chloride*, b. p. 80—85°/12 mm. *βζ-Dimethyl-*Δ^{ϵ}*-heptene-γ-carboxylic acid*, from dimethylallyl bromide and ethyl *iso*propylmalonate, is a colourless oil, b. p. 140—145°/12 mm.; *chloride*, b. p. 115°/10 mm. *β-Methyl-*$\Delta^{\beta\eta}$*-octadiene-ε-carboxylic acid*,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH{:}CH_2,$$

colourless oil, b. p. 137—138°/10 mm., is obtained from dimethylallyl bromide and ethyl allylmalonate; *chloride*, b. p. 84°/10 mm.

E. H. R.

Modification of the Sandmeyer Synthesis of Nitriles. H. T. CLARKE and R. R. READ (*J. Amer. Chem. Soc.*, 1924, **46**, 1001—1003).—A method of preparing nitriles which avoids the evolution of hydrogen cyanide is described. The diazonium solution is neutralised by means of sodium carbonate at 0—4° and poured into a similarly cooled solution of sodium cuprocyanide, the surface of which is first covered with a layer of benzene. With good stirring, the benzene (in which the nitrile is soluble) is drawn beneath the surface and a rise in temperature prevented. Yields of nitriles up to 60—70% of the theoretical were obtained using aniline, *o*-toluidine, *p*-toluidine, and other amines. In the absence of the benzene, the reaction product comes to the surface as a dark brown oil, in which, after a few moments, a vigorous action is set up and fumes smelling of phenylcarbylamine are given off. A. C.

Electrochemical Reductions in Acid Solution. K. KINDLER, O. GIESE, and A. ISBERG (*Ber.*, 1924, **57**, [*B*], 773—775).—An examination of the reduction of phenylacetamide, phenylthioacetamide, and their *N*-alkyl derivatives shows that the more *N*-methyl groups there are present the more rapid is the electrochemical reduction and the slower the reduction by aluminium amalgam. The figures in brackets give the percentage of the theoretical yield of amine formed by reduction of the corresponding amide. (I) Electrochemical reduction (cf. A., 1923, i, 568, 1090): $CH_2Ph{\cdot}CO{\cdot}NH_2$ (<1%); $CH_2Ph{\cdot}CO{\cdot}NHMe$ (80%); $CH_2Ph{\cdot}CO{\cdot}NMe_2$ (92%); $CH_2Ph{\cdot}CS{\cdot}NHMe$ (80%); $CH_2Ph{\cdot}CS{\cdot}NMe_2$ (100%). No phenylacetaldehyde was observed as a by-product. (II) Reduction with aluminium amalgam: $CH_2Ph{\cdot}CS{\cdot}NH_2$ (74%); $CH_2Ph{\cdot}CS{\cdot}NHMe$ (2%); $CH_2Ph{\cdot}CS{\cdot}NMe_2$ (<1%). During the electrolysis of an aqueous-alcoholic hydrochloric acid solution of phenylacetdimethylamide, its concentration around the cathode increased, whereas with phenylacetamide no such increase was noted. It is suggested that during electrolysis of the strongly acid solution the first stage is the addition of acid to form the ammonium or oxonium salts, the cations of which, after giving up their charge, are converted into free radicals which then readily undergo reduction at the cathode. F. A. M.

Syntheses by means of Sodamide. Preparation of Benzyl Phenylalkylacetates and the Corresponding Acids. (MME.) RAMART and A. HALLER (*Compt. rend.*, 1924, **178**, 1583—1587; cf. this vol., i, 171, 286).—At the ordinary temperature, the action of sodamide on phenyl formate yields sodium phenoxide, ammonia, and carbon monoxide, and on phenyl acetate, sodium phenoxide and acetamide. Treatment of benzyl *iso*butyrate in xylene solution with sodamide and then with benzyl chloride yields *N*-benzyl*iso*butyramide and another compound, m. p. 65—66°, of unknown constitution.

With benzyl phenylacetate, a similar reaction occurs, the temperature gradually rising and phenylacetamide and phenylacetbenzylamide being formed. If, however, the reaction is carried out at 0° and the flask is connected through a reflux condenser with a vacuum pump so as to facilitate the disengagement of ammonia, little amide is formed but instead the sodium derivative of the ester, $C_7H_7{\cdot}O{\cdot}CO{\cdot}CHPhNa$ or $C_7H_7{\cdot}O{\cdot}C(ONa){:}CHPh$; when the evolution of ammonia becomes very slight, the alkyl or benzyl halide is added gradually, the product being finally treated with water and the mixture of esters rectified in a vacuum.

Benzyl α-phenylpropionate (hydratropate), formed under these conditions, could not be separated from the benzyl phenylacetate, but is readily separated as acid (cf. Fittig and Wurster, A., 1879, 379). *Benzyl phenylallylacetate*, similarly obtained, forms an oil, b. p. 210—212°/25 mm. (cf. Buddeberg, A., 1890, 1142). *Benzyl benzylphenylacetate* is a yellow, oily liquid, b. p. 250—255°/18 mm.

T. H. P.

Higher Terpene Compounds. XXII. *l*-Pimaric Acid. L. RUZICKA, F. BALAS, and F. VILIM (*Helv. Chim. Acta*, 1924, **7**, 458—471).—Improved methods for obtaining *l*-pimaric acid from galipot are described, consisting in fractionally crystallising the resinic acids from acetone, a procedure which may be preceded by fractional crystallisation of the sodium salts (cf. Dupont, A., 1921, i, 510). *l*-Pimaric acid is more stable in the form of its sodium salt than *d*-pimaric acid. Hydrogenation experiments show that *l*-pimaric, like abietic acid, has two double bonds (cf. A., 1923, i, 818). *Dihydro*-l-*pimaric acid* is obtained by hydrogenation of *l*-pimaric acid with colloidal platinum and hydrogen in ethyl acetate; it consists apparently of a mixture of isomerides, the first fraction of which, from alcohol, forms crystals, m. p. 142—144°, $[\alpha]_D$ +24° in 1% alcoholic solution. More energetic hydrogenation by the method of Willstätter and Waldschmidt-Leitz (A., 1921, ii, 185) resulted in the formation of *tetrahydro*-l-*pimaric acid*, a mixture of isomerides, m. p. 120—160°. The molecular refractions of the esters of *l*-pimaric acid also indicate the presence of two double bonds; the *methyl* ester is a viscous oil, b. p. 166—169°/0·5 mm., $[\alpha]_D$ —190·36° in 5% alcoholic solution, d_4^{22} 1·0312; n_D^{22} 1·5232; when kept, the oil formed long crystals, m. p. 57°; the *ethyl* ester also a viscous oil, b. p. 175—177°/0·5 mm., $[\alpha]_D$ —170·9° in 6% alcoholic solution, d_4^{23} 1·0124; n_D^{23} 1·5153.

When *l*-pimaric acid is heated in boiling acetic acid, an isomeride is formed, m. p. 167—168°, $[\alpha]_D$ −103·7°, corresponding in crystalline form with abietic acids from various sources, whilst by heating at 300° it is converted into an isomeride, m. p. 175—176°, $[\alpha]_D$ +22·3°, corresponding with abietic acid from American colophony, m. p. 178—179°, $[\alpha]_D$ +3° (A., 1922, i, 547). It is concluded, therefore, that *l*-pimaric acid belongs to the group of spatially isomeric abietic acids. *d*-Pimaric acid is a structural isomeride and does not belong to the abietic acid group. In agreement with this view, *l*-pimaric acid gives retene when dehydrogenated with sulphur, and resembles abietic acid in other respects. E. H. R.

***iso*Fenchocarboxylic Acid.** S. NAMETKIN and A. RUSCHENTZEV (*J. pr. Chem.*, 1923, **106**, 39—40).—The acid is prepared by passing dry carbon dioxide into a cold solution of *iso*fenchone in ether in the presence of sodium wire. After the vigorous reaction has subsided, the mixture is heated for 3 days. The ether is then evaporated, excess of sodium removed, and the residue decomposed by water. The viscid residual mass is washed with ether, acidified with sulphuric acid, and the acid purified through its sodium salt. It melts at 87—88° with evolution of carbon dioxide. With ferric chloride, it yields a dark blue coloration, rapidly turning dirty green. The acid decomposes rapidly, even in the dark, yielding *iso*fenchone and a white solid, m. p. 230—231°. F. G. P.

Action of Sodium Hydrogen Sulphite on Chlorides of the Hydroximic Acids. VII. C. GASTALDI (*Gazzetta*, 1924, **54**, 220—226).—The ready replacement of the chlorine atom by hydroxyl observed when chloroximinoacetone is treated with sodium hydrogen sulphite (cf. A., 1923, i, 1236) occurs also in other similar cases and furnishes a means of preparing hydroxamic acids not obtainable by the ordinary methods.

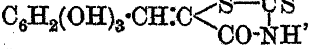
Benzoylformhydroxamic acid, COPh·CO·NH·OH or

OH·CBz:NOH,

prepared from α-chloro-α-oximinoacetophenone, forms stable, colourless prisms or pink laminæ, m. p. 117° (decomp.), and forms two *oximes*: (1) the *α-modification*, NOH:CPh·CO·NH·OH or NOH:CPh·C(OH):NOH, crystallises in colourless prisms, m. p. 177° (decomp.), and in aqueous solution gives with nickel acetate and ammonia a green precipitate soluble in dilute acetic acid; (2) the *β-modification*, prepared by the action of sodium hydrogen sulphite on benzoylformhydroximic chloride oxime (chlorophenylglyoxime) (cf. Ponzio and Avogadro, A., 1923, i, 472), forms pale yellow laminæ, m. p. 189° (decomp.), and differs from the α-form in giving with nickel acetate a brick-red precipitate insoluble in dilute acetic acid or ammonia solution. *Benzoylformhydroxamic acid phenylhydrazone*, $C_{14}H_{13}O_2N_3$, crystallises in yellow needles, m. p. 127°. T. H. P.

3 : 4 : 5-Trihydroxycinnamic Acid and the Mechanism of Knoevenagel's Cinnamic Acid Synthesis. K. W. ROSENMUND and T. BOEHM (*Annalen*, 1924, **437**, 125—147).—Gallaldehyde on warming with one or two mols. of aniline and malonic acid in alcoholic solution yields a yellow solid which on heating at 155—160° melts with evolution of carbon dioxide. Treatment with hydrochloric acid converts the substance into the known hydrochloride of gallaldehyde-aniline, an additive compound, not a Schiff's base. The yellow solid proves to be a normal malonate of the aldehyde-aniline, $[C_6H_2(OH)_3\cdot CH(OH)\cdot NHPh]_2,CH_2(CO_2H)_2$, and the expected trihydroxycinnamic acid could not be obtained from this reaction. Protocatechualdehyde behaves similarly, and these results suggest that the primary product in the reaction is not a benzylidenemalonic acid, as Knoevenagel suggested (A., 1899, i, 144), but a benzylideneaniline (cf. Dimroth and Zoeppritz, A., 1902, i, 292). These additive products form stable salts with strong acids (cf. Dimroth, A., 1902, i, 292), and do not react with malonic acid to give substituted acrylic acids. The Schiff's bases do not form stable salts, but react with malonic acid, yielding substituted acrylic acids. The formation of acrylic acid derivatives is thus conditional on the existence of a double bond between carbon and nitrogen, and it is suggested that the malonic acid attacks the molecule at this point: $CHPh\colon NPh + CH_2(CO_2H)_2 \longrightarrow NHPh\cdot CHPh\cdot CH(CO_2H)_2$. The resulting β-anilinodicarboxylic acid is unstable (cf. Goldstein, A., 1895, i, 470; 1896, i, 435) and easily loses carbon dioxide, yielding a β-substituted β-anilinopropionic acid, *e.g.*, $NHPh\cdot CHPh\cdot CH_2\cdot CO_2H$, which is decomposed by mineral acid, yielding aniline and the corresponding acrylic acid. On this theory, the failure of attempts to prepare trihydroxycinnamic acid from gallaldehyde, aniline, and malonic acid is attributed to the weakly basic character of aniline as opposed to the relatively acidic gallaldehyde. When instead of aniline, the stronger base piperidine was used, 3 : 4 : 5-trihydroxycinnamic acid was obtained in good yield.

Attempts were also made to prepare trihydroxycinnamic acid by condensing gallaldehyde with malonic acid derivatives. Ethyl malonate and cyanoacetic acid gave no result, but with malononitrile gallaldehyde yields ββ-*dicyano*-3 : 4 : 5-*trihydroxystyrene*, $C_6H_2(OH)_3\cdot CH\colon C(CN)_2$, m. p. 250° (decomp.), which by acid hydrolysis is converted into α-cyano-3 : 4 : 5-trihydroxycinnamamide, $C_6H_2(OH)_3\cdot CH\colon C(CN)\cdot CO\cdot NH_2$. On further hydrolysis, this yields α-cyano-3 : 4 : 5-trihydroxycinnamic acid, but the hydrolysis of the second cyano group could not be effected. Condensation of gallaldehyde with rhodanine gave a trihydroxybenzylidenerhodanine,

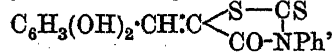


$C_6H_2(OH)_3\cdot CH\colon C<\begin{matrix}S—CS\\ CO\cdot NH\end{matrix}$, but attempts to prepare from this α-thioltrihydroxycinnamic acid were unsuccessful.

ββ-*Dicyano*-3 : 4 : 5-*triacetoxystyrene* (from triacetylgallaldehyde and malononitrile) has m. p. 139—140°. ββ-*Dicyano*-3 : 4-*dihydroxystyrene* forms yellow needles, m. p. 221° (decomp.); *acetyl* derivative, m. p. 110—111°. Hydrolysis with 38% hydrochloric acid converts [illegible] dicyanotrihydroxystyrene into α-cyano-3 : 4 : 5-trihydroxy-[illegible], reddish-yellow needles, m. p. 268° (decomp.), which [illegible] by condensation of gallaldehyde with cyanoacet-[illegible] derivative, m. p. 210—211°. α-*Cyano*-3 : 4-*di*-

acetoxycinnamamide has m. p. 196—198°. Condensation of gallaldehyde with ethyl cyanoacetate in the presence of sodium ethoxide yields *ethyl α-cyano-3 : 4 : 5-trihydroxycinnamate*, yellow needles, m. p. 201—202° (*triacetyl* derivative, m. p. 142°), which on careful hydrolysis with dilute sodium hydroxide yields *α-cyano-3 : 4 : 5-trihydroxycinnamic acid*, small, pale yellow plates, m. p. 210—212° (decomp.); *triacetyl* derivative, m. p. 180°. Protocatechualdehyde similarly yields *ethyl α-cyano-3 : 4-dihydroxycinnamate*, yellow needles, m. p. 168° (*diacetyl* derivative, m. p. 97°), which by alkaline hydrolysis gives *α-cyano-3 : 4-dihydroxycinnamic acid* (*α-cyanocaffeic acid*), yellow plates, m. p. 224—225° (decomp.); *diacetyl* derivative, m. p. 195—196°.

Gallaldehyde condensed with rhodanine in the presence of sodium hydroxide yields amorphous 3 : 4 : 5-*trihydroxybenzylidenerhodanine*, which gives a crystalline *triacetyl* compound, m. p. 222—223°. Similarly, protocatechualdehyde and rhodanine (in alcoholic sulphuric acid) yield 3 : 4-dihydroxybenzylidenerhodanine, small, yellowish-brown tablets, m. p. 270—280° (decomp.); *diacetyl* derivative, m. p. 217—218°. Phenylrhodanine gives *phenyl-3 : 4-dihydroxybenzylidenerhodanine*,



$C_6H_3(OH)_2\cdot CH{:}C<\begin{matrix}S—CS\\ CO\text{-}NPh\end{matrix}$,

dense yellow lances, m. p. 268—270° (decomp.); *diacetyl* derivative, m. p. 195°. Gallaldehyde and aniline in alcoholic solution give with hydrogen chloride a yellow precipitate of *gallaldehydeaniline* (*hydroxy-3 : 4 : 5-trihydroxyphenylmethylaniline*) *hydrochloride*, $C_6H_2(OH)_3\cdot CH(OH)\cdot NHPh,HCl$, m. p. 226°, which does not lose water at 130°. The free *base* crystallises in yellow needles ($+1H_2O$), which lose water at 80° and melt at 190—192°, yielding the Schiff's base, 3 : 4 : 5-*trihydroxybenzylideneaniline*, which on warming with hydrochloric acid is reconverted into the gallaldehydeaniline hydrochloride. The *malonate* (*supra*) forms yellow needles, m. p. 171°. *Protocatechualdehydeaniline hydrochloride* forms fine, yellowish-brown needles, m. p. 231—232°; *malonate*, m. p. 173°.

3 : 4 : 5-*Trihydroxycinnamic acid* forms colourless needles ($+1H_2O$), m. p. 207—208°; the water is lost at 120°; *triacetyl* derivative, needles, m. p. 168°. The acid is distinguished from gallic acid and gallaldehyde by its ferric chloride reaction (dark green coloration, changing to clear yellow on dilution) and by the fine carmine-red to violet coloration produced with potassium cyanide. With bromine (2 mols.) in acetic acid solution, the trihydroxycinnamic acid yields a *dibromo* derivative, $C_9H_6O_5Br_2$, colourless needles, m. p. 186—187°, probably 2 : 6-dibromo-3 : 4 : 5-trihydroxycinnamic acid. The triacetyl derivative similarly yields the corresponding *dibromotriacetoxycinnamic acid*, $C_{15}H_{12}O_8Br_2$, long tablets, m. p. 183°. R. B.

Preparation of *p-iso*Propylphenylacetaldehyde and some of its Isomerides and Homologues. P. Chuit and J. Bolle (*Bull. Soc. chim.*, 1924, [iv], **35**, 200—205).—*p-iso*Propylphenylacetaldehyde (cf. A., 1923, i, 1101) may be prepared as a colourless liquid, b. p. 116·5—117°/11 mm., d^{15} 0·980, n_D^{20} 1·51071, by condensing cumaldehyde with ethyl chloroacetate in presence of sodium ethoxide. The product is hydrolysed and then steam-distilled in presence of excess of oxalic acid solution. The semicarbazone melts at 172°, not at 181° (cf. Bert, *loc. cit.*). The aldehyde polymerises to a viscous oil on standing. In a similar manner, from 2 : 4 : 6-trimethylbenzaldehyde, 2 : 4 : 6-*trimethylphenylacetaldehyde* is obtained, m. p. 61°, b. p. 137—140°/13 mm., having a faint disagreeable odour. 3 : 4 : 6-*Trimethylphenylacetaldehyde* is a colourless liquid, b. p. 127—129°/15 mm., d^{15} 0·998, n_D^{15} 1·5311; *semicarbazone*, m. p. 191°.

By the condensation of ethyl chloroglyoxylate with *p*-cymene in presence of aluminium chloride, ethyl cymylglyoxylate is formed (b. p. 175—180°/12 mm.) which, on conversion into the acid and boiling with excess of aniline, forms the phenylimide (b. p. 200—202°/14 mm.). By warming the latter with dilute hydrochloric acid, 6-*methyl*-3-iso*propylbenzaldehyde* is obtained, a colourless liquid, b. p. 121—121·3°/14 mm., d^{15} 0·978, n_D^{15} 1·5108. Condensation of this with chloroacetic acid as above yields 2-p-*cymylacetaldehyde*, b. p. 128·5—129°/13 mm., d^{15} 0·967, n_D^{15} 1·5175; *semicarbazone*, m. p. 160°.

Poor yields of m-*cymylaldehyde* (2-*methyl*-4-iso*propylbenzaldehyde*) are obtained from *m*-cymene by Gattermann's synthesis. It is a liquid, b. p. 115—118°/13 mm., d^{15} 0·972; *semicarbazone*, m. p. 198—199°. It oxidises in air to a steam-volatile cymylcarboxylic acid, m. p. 77·5°, which is also one product of oxidation by boiling dilute nitric acid. The other product is 3-methylterephthalic acid, the formation of which proves the constitution of the original compound. 2-m-*Cymylacetaldehyde*, prepared by the above general method, is a colourless liquid, b. p. 123—126°/12 mm., d^{15} 0·973, n_D^{15} 1·5203, *semicarbazone*, m. p. 158—159°. E. E. T.

Isomerisation of Nitroaldehydes by Chemical Means. G. HELLER (*J. pr. Chem.*, 1923, **106**, 1—16).—*o*-Nitrobenzaldehyde on exposure to light in indifferent solvents is converted into *o*-nitrosobenzoic acid, in alcoholic solution into the related esters. Similarly, on exposure to light in absolute hydrocyanic acid, the nitrosobenzoic acid results, whilst *o*-nitromandelonitrile under the same conditions loses hydrogen cyanide and gives the acid. The question whether oxygen can be thus transferred from the nitro to the aldehyde group by chemical methods has not been satisfactorily settled. It has been found that potassium cyanide reacts with an aqueous-alcoholic solution of *o*-nitrobenzaldehyde readily in the cold, necessitating external cooling, *o*-nitrosobenzoic acid being found in the reaction product, and ammonium *o*-nitrosobenzoate is obtained by dissolving *o*-nitromandelonitrile in alcoholic ammonia. The conversion of *o*-nitrobenzaldehyde into the nitrosobenzoic acid without isolating the nitromandelonitrile is best accomplished by the action of a solution of potassium cyanide and ammonium acetate in concentrated ammonia on an alcoholic [illegible] *o*-nitrobenzaldehyde, almost pure ammonium nitroso[illegible] precipitated. *o*-Nitromandelonitrile is probably first produced by the action of potassium cyanide, and loses hydrogen cyanide, forming *o*-nitrosobenzoic acid at the same time. Ekecrantz and Ahlqvist (A., 1908, i, 347) by the action of potassium cyanide on a hot alcoholic solution of the *o*-nitroaldehyde obtained azoxybenzoic acid and nitrosobenzoic acid, but since alkali does not act so smoothly on *o*-nitromandelonitrile as ammonia does, their investigation could not lead to a homogeneous result. By altering the conditions, it is found that small quantities of azoxybenzoic acid may be obtained. *o*-Nitropiperonal can be converted into the mandelonitrile by the action of potassium cyanide on its hydrogen sulphite compound, the nitrile produced yielding the nitroso-acid on treatment with alcoholic ammonia, or by the direct action of the alcoholic ammoniacal ammonium cyanide solution on the nitroaldehyde. The ammonium cyanide acts as an oxygen carrier since less than 1 mol. is sufficient. 2-Nitro-5-chlorobenzaldehyde and the corresponding 5-bromoaldehyde are readily converted into the nitroso-acids. Nitrohydroxyaldehydes give only resinous products, as do *o*-nitrovanillin and nitroterephthalaldehyde. In all these cases also, no cyanohydrin could be obtained from the aldehyde. 2 : 4-Dinitrobenzaldehyde reacts normally with ammonium cyanide to give 4-nitro-2-nitrosobenzoic acid, but by the action of potassium cyanide in glacial acetic acid solution yields 2-nitro-4-nitrosobenzoic acid. No analogous compounds were obtained from trinitrobenzaldehyde. Attempts to carry out the reaction with such substances as β-*o*-nitrophenyllactonitrile, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH(OH)CN$, and γ-*o*-nitrocinnamylglycollonitrile, $NO_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CH(OH)CN$, gave negative results either with the nitriles themselves or with the parent nitroaldehydes. Oxygen is therefore not capable of migrating into the side chain from a neighbouring nitro group. *o*-Nitrophenyl-lactonitrile has been converted into the acid amide by hydrolysis with 75% sulphuric acid, and the amide into the acid by heating with concentrated sulphuric acid and glacial acetic acid. By reduction of the acid with zinc dust and hydrochloric acid, 3-hydroxycarbostyril is produced.

m-Nitroaldehydes behave quite differently, yielding only amorphous products. 2-Chloro-5-nitrobenzaldehyde in glacial acetic acid solution yields a cyanohydrin, but from this only a compound of complex type was obtained by the use of the alcoholic ammoniacal ammonium cyanide solution. With *p*-nitrobenzaldehyde, an amorphous product was obtained.

A repetition of the work of Ekecrantz and Ahlqvist (*loc. cit.*) showed that *o*-nitrobenzaldehyde in the presence of a small quantity of potassium cyanide does not yield azoxybenzoic acid, but that *o*-nitrosobenzoic acid and a compound, $C_{14}H_8O_6N_2$ (in very small yield), m. p. 162—163°, are produced. On the other hand, by increasing the amount of potassium cyanide, *o*-nitrosobenzoic acid, the compound $C_{14}H_8O_6N_2$, and azoxybenzoic acid are obtained.

[With H. KRETZSCHMANN.]—o-*Nitropiperonalcyanohydrin*, $C_9H_6O_5N_2$, crystallises in pale yellow needles, m. p. 119°. o-*Nitrosopiperonylic acid*, $C_8H_5O_5N$, a yellow, crystalline powder, sinters at 160—165°, and melts at about 198°.

[With H. GRUNDMANN.]—5-*Bromo*-2-*nitrosobenzoic acid* crystallises in pale brown needles, m. p. 173°. 4-*Nitro*-2-*nitrosobenzoic acid*, $C_7H_4O_5N_2$, from 2 : 4-dinitrobenzaldehyde, has m. p. above 300°; its *methyl* ester crystallises in silky needles, m. p. 137° to a green liquid. 2-*Nitro*-4-*nitrosobenzoic acid* is a yellow, crystalline solid, m. p. about 230°. On oxidation with fuming nitric acid, it yields dinitrobenzoic acid. Its *methyl* ester crystallises in yellow needles, m. p. 141° to a green liquid. β-o-*Nitrophenyl-lactonitrile*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH(OH)CN$, from the hydrogen sulphite compound of *o*-nitrophenylacetaldehyde, crystallises in plates, m. p. 70—71°. On hydrolysis with 75% sulphuric acid, it is converted into the *lactamide*, $C_9H_{10}O_4N_2$, needle aggregates, m. p. 195°. By heating the lactamide in glacial acetic acid with excess of concentrated sulphuric acid, o-*nitrophenyl-lactic acid* is obtained, nearly colourless needles, m. p. 72°.

[With H. JÜRGENS.]—o-*Nitrocinnamylglycollonitrile*, $C_{10}H_8O_3N_2$, obtained by the action of absolute hydrocyanic acid on *o*-nitrocinnamaldehyde, has m. p. 79°. By the action of alcoholic ammonia, hydrocyanic acid is eliminated and tarry products are obtained. Dilute solutions of sodium hydroxide regenerate the aldehyde.

[With K. MÜLLER-BARDOFF.]—2-*Chloro*-5-*nitromandelonitrile*, obtained by the action of potassium cyanide on a glacial acetic acid solution of the corresponding aldehyde, crystallises in scales, m. p. 124°. Alcoholic ammonia converts it into a complex, crystalline substance, m. p. 303°, containing 15·4% N, insoluble in acids and alkalis and scarcely soluble in any of the organic solvents.

F. G. P.

Mercuration of Nitrohydroxybenzaldehydes. T. A. HENRY and T. M. SHARP (*J. Chem. Soc.*, 1924, **125**, 1049—1060; cf. A., 1923, i, 726).—The previously described *m*-hydroxyacetoxymercuribenzaldehyde (T., 1922, **121**, 1059) is now shown to be the 2-acetoxymercuri compound, from its conversion into 2-nitro-3-hydroxybenzaldehyde and into an iodo-*m*-hydroxybenzaldehyde yielding 2 : 3-dihydroxybenzoic acid on heating with sodium hydroxide.

The work has been extended to the nitrobenzaldehydes, which did not yield mercury derivatives, and to the nitrohydroxybenzaldehydes. The mercuration is effected by boiling with mercuric acetate and a small amount of acetic acid in 50% alcoholic solution. The dimercuri compounds obtained from 6-nitro-, 4-nitro-, and 2-nitro-3-hydroxybenzaldehyde on treatment with bromine all yield 2 : 4-dibromo-6-nitro-3-hydroxybenzaldehyde, the nitro groups in the 2 and 4 positions changing places with the bromine atom, which replaces mercury in position 6. The reaction with iodine is normal.

Mercuration of 3-nitro-4-hydroxybenzaldehyde yields only [illegible]-4-*hydroxy*-5-*hydroxymercuribenzaldehyde*, small orange plates, [illegible] 265°, but not melting at 300°, which by solution in [illegible] and precipitation with hydrochloric acid is converted into 3-*nitro*-4-*hydroxy*-5-*chloromercuribenzaldehyde*, colourless needles, m. p. 226° (decomp.), and on crystallisation from acetic acid yields 3-*nitro*-4-*hydroxy*-5-*acetoxymercuribenzaldehyde*, colourless prisms, darkening at 250°. With iodine in potassium iodide solution, the hydroxymercuri compound yields 5-*iodo*-3-*nitro*-4-*hydroxybenzaldehyde*, yellow plates, m. p. 171—172°. Similarly, 6-nitro-3-hydroxybenzaldehyde yields first an orange solid, apparently a mixture of the diacetoxydimercuri and dihydroxydimercuri compounds, whilst from the mother-liquors mixtures of mono- and di-mercurated products are obtained. The orange solid by crystallisation from propionic acid is converted into 6-*nitro*-3-*hydroxy*-2 : 4-*dipropoxydimercuribenzaldehyde*, orange-yellow needles, exploding at 235°. Its solution in sodium hydroxide on treatment with hydrochloric acid precipitates 6-*nitro*-3-*hydroxy*-2 : 4-*dichlorodimercuribenzaldehyde*, colourless needles. The pale yellow 6-*nitro*-3-*hydroxychloromercuribenzaldehyde* obtained from the more soluble fractions decomposes at 198°, and with iodine solution yields an *iodo*-6-*nitro*-3-*hydroxybenzaldehyde*, yellow prisms, m. p. 206° (decomp.), and a small quantity of 2 : 4-*di-iodo*-6-*nitro*-3-*hydroxybenzaldehyde*, yellow prisms or needles, m. p. 142° (decomp.); *semicarbazone*, m. p. 214° (decomp.); *oxime*, m. p. 207—208° (decomp.). The di-iodo compound is formed almost quantitatively by the action of iodine on the dimercuri compound, a small quantity of a mercuric iodide additive *compound*, $2C_7H_3O_4NI_2,HgI_2$, m. p. 184° (decomp.), being also sometimes formed, and this on decomposition with hydrogen sulphide yields mercuric sulphide and 2 : 4-di-iodo-6-nitro-3-hydroxybenzaldehyde. The dimercurated compound on treatment with bromine in alcoholic solution yields 2 : 4-*dibromo*-6-*nitro*-3-*hydroxybenzaldehyde*, colourless prisms, m. p. 152·5° (decomp.), which on oxidation with alkaline permanganate is converted into 2 : 4-*dibromo*-6-*nitro*-3-*hydroxybenzoic acid*, colourless needles, m. p. 230° (decomp.), identical with the acid obtained by oxidising 2 : 4-dibromo-6-nitro-*m*-cresol.

4-Nitro-3-hydroxybenzaldehyde on mercuration yields an orange-coloured 4-*nitro*-3-*hydroxy-hydroxymercuriacetoxymercuribenzaldehyde*, which on crystallisation from formic acid is converted into 4-*nitro*-3-*hydroxy*-2 : 6-*diformoxydimercuribenzaldehyde*, pale yellow needles, darkening at 120°, exploding at 257°. From its solution in potassium hydroxide, hydrochloric acid precipitates 4-*nitro*-3-*hydroxy*-2 : 6-*dichlorodimercuribenzaldehyde*, pale yellow needles ($+1H_2O$), darkening at 240° (the anhydrous substance decomposes at 282°) and carbon dioxide precipitates 2 : 3-*anhydro*-4-*nitro*-3-*hydroxy*-2 : 6-*dihydroxydimercuribenzaldehyde*. From the more soluble fractions of the mercuration product, by extraction with formic acid, 4-*nitro*-3-*hydroxyformoxymercuribenzaldehyde*, m. p. 233—235°, is obtained. The 4-*nitro*-3-*hydroxypropoxymercuribenzaldehyde*, pale orange needles, and the 4-*nitro*-3-*hydroxychloromercuribenzaldehyde*, yellow powder, decomposing at 187°, were also prepared. Treatment with iodine converts the monomercurated compound into an *iodo*-4-*nitro*-3-*hydroxybenzaldehyde*, yellow needles, m. p. 185°. The dimercurated compound, on treatment with bromine, yields the 2 : 4-dibromo-6-nitro-3-hydroxybenzaldehyde previously obtained from the dimercuri-6-nitrohydroxybenzaldehyde. 2 : 6-*Dibromo-4-nitro-3-hydroxybenzoic acid*, m. p. 209°, was obtained, together with 4 : 6-dibromo-2-nitrophenol, by the oxidation of 2 : 6-dibromo-4-nitro-*m*-cresol with alkaline potassium ferricyanide. On treatment with iodine solution, the dimercurated substance yields a *di-iodo-4-nitro-3-hydroxybenzaldehyde*, yellow needles, m. p. 122°, which on oxidation gives a *di-iodo-4-nitro-3-hydroxybenzoic acid*, yellow prisms, m. p. 249° (decomp.). This acid is identical with that obtained by oxidising with alkaline potassium ferricyanide the di-iodo-4-nitro-*m*-cresol (which by analogy should be the 2 : 6-di-iodo derivative) prepared by treating 4-nitro-*m*-cresol with iodine and mercuric oxide.

The mercuration of 2-nitro-3-hydroxybenzaldehyde similarly yields at first mainly 2-*nitro-3-hydroxyhydroxymercuriacetoxymercuribenzaldehyde*, yellow amorphous, and then 2-*nitro-3-hydroxydiacetoxydimercuribenzaldehyde*, pale yellow needles, from which the 2-*nitro-3-hydroxydichlorodimercuribenzaldehyde*, pale green, gelatinous substance, decomp. at 236°, is obtained. From the mother-liquors by fractional crystallisation from acetic acid, 2-*nitro-3-hydroxyacetoxymercuribenzaldehyde*, microscopic needles, was obtained. 2-*Nitro-3-hydroxychloromercuribenzaldehyde*, yellow powder, decomposes at 207°. On treatment with bromine, the dimercurated substance gives 2 : 4-dibromo-6-nitro-3-hydroxybenzaldehyde, and on shaking with excess of iodine solution a di-iodo compound is obtained, bright yellow needles, m. p. 154·5°, which is probably 4 : 6-*di-iodo-2-nitro-3-hydroxybenzaldehyde*. The crude monomercurated product similarly yields an iodo compound, m. p. about 110°, probably iodo-2-nitro-3-hydroxybenzaldehyde, together with some di-iodo compound, m. p. 154·5°.

The bactericidal action of the new substances has been investigated. R. B.

Isomerism of the Oximes. XVII. Some Bromo- and Nitro-substituted Mono- and Di-methoxybenzaldoximes. O. L. Brady and L. B. Manjunath (*J. Chem. Soc.*, 1924, **125**, 1060—1068; cf. T., 1916, **109**, 650; 1920, **117**, 1040; 1923, **123**, 2434).—A continuation of previous work on the influence of negative groups on the stability of isomeric benzaldoximes. Ciusa's work (A., 1907, i, 137) on 3-nitro-*p*-methoxybenz*anti*aldoxime and its *syn*-isomeride has been confirmed. The conversion of the *anti*-isomeride into the *syn*-compound was effected by pouring a suspension of the *anti*-oxime in hydrochloric acid into sodium carbonate solution. The m. p. of the *anti*-oxime is 166° and of the *syn*-oxime 164—166°. *Acetyl-3-nitro-*p*-methoxybenz*syn*aldoxime*, colourless needles, m. p. 115°, on decomposition with sodium hydroxide [illegible] -methoxybenzonitrile. The *N*-benzyl ether melts [illegible] (cf. Ciusa, *loc. cit.*). The N-*methyl ether*, yellow prisms, [illegible] *O-methyl ether* of the *anti*-oxime, m. p. 120°, *carb*-[illegible] *benz*anti*aldoxime*, m. p. 128° (decomp.), [illegible] *methoxybenz*syn*aldoxime*, m. p. 117° (decomp.), are described. On hydrolysis with sodium hydroxide, the carbanilino derivative of the *anti*-oxime yields the original oxime, whereas the isomeric carbanilino derivative yields aniline and 3-nitro-*p*-methoxybenzonitrile on warming, and on prolonged boiling, ammonia and 3-nitro-*p*-methoxybenzoic acid with a little 3-nitro-*p*-methoxybenz*anti*aldoxime.

3-Bromo-*p*-methoxybenzaldehyde, obtained by bromination of *p*-methoxybenzaldehyde in acetic acid solution in the presence of iodine, readily yields *3-bromo-*p*-methoxybenz*anti*aldoxime*, m. p. 118° (*acetyl* derivative, m. p. 82°, hydrolysed to the sodium salt of the original oxime with sodium hydroxide), which on boiling with excess of acetic anhydride is converted into *3-bromo-*p*-methoxybenzonitrile*, m. p. 122°. The following derivatives of 3-bromo-*p*-methoxybenz*anti*aldoxime were prepared: O-*benzyl ether*, m. p. 82°; O-*methyl ether*, m. p. 76°; *phenylcarbimide* derivative, m. p. 92°, hydrolysed mainly to the original oxime, some diphenylcarbamide being also formed. The *anti*-oxime is readily converted by the hydrochloric acid method (*supra*) into *3-bromo-*p*-methoxybenz*syn*aldoxime*, m. p. 134° [N-*benzyl ether*, m. p. 151°; N-*methyl ether*, m. p. 108°; *phenylcarbimide* derivative, m. p. 104° (decomp.), yielding ammonia and 3-bromo-*p*-methoxybenzoic acid on hydrolysis], which with cold acetic anhydride and sodium carbonate solution is converted into 3-bromo-*p*-methoxybenzonitrile. The 5-nitro-*o*-methoxybenzaldoxime, m. p. 183°, prepared by Schnell (A., 1884, 1164), is shown to be the *anti*-oxime, its *acetyl* derivative, m. p. 160°, yielding the original oxime on hydrolysis. In a similar manner, 6-nitro-3 : 4-dimethoxybenzaldoxime (A., 1900, i, 178) (*acetyl* derivative, yellow leaflets, m. p. 152°) is shown to be the *anti*-oxime. 5-Nitro-3 : 4-dimethoxybenzaldehyde, obtained from 5-nitrovanillin by methylation with diazomethane (excess of the reagent yields *5-nitro-3 : 4-dimethoxyacetophenone*, m. p. 89°), or by treatment of the silver salt with methyl iodide, yields *5-nitro-3 : 4-dimethoxybenz*anti*aldoxime*, m. p. 151° (*acetyl* derivative, m. p. 115°, yielding the oxime on hydrolysis). 6-Bromo-3 : 4-dimethoxybenzaldoxime (Pschorr, A., 1912, i, 775) yields an *acetyl* derivative, m. p. 140°, regenerating the original oxime on hydrolysis and accordingly has the *anti*-structure. Attempts to prepare *syn*-isomerides from 5-nitro-*o*-methoxybenz*anti*aldoxime, 6-nitro-, 6-bromo-, and 5-nitro-3 : 4-dimethoxybenz*anti*aldoximes were unsuccessful, and in all these cases solutions of the oximes in organic solvents yielded no hydrochloride on treatment with hydrogen chloride (cf. T., 1923, **123**, 1783). R. B.

Isomerism of the Oximes. XVIII. Action of Chloro-2 : 4-dinitrobenzene on some Isomeric Aldoximes. O. L. Brady and R. Truszkowski (*J. Chem. Soc.*, 1924, **125**, 1087—1096; cf. T., 1922, **121**, 2106).—Chloro-2 : 4-dinitrobenzene reacts readily in alcoholic solution with the sodium salts of substituted benz*anti*aldoximes yielding dinitrophenyl ethers, to which the *syn*-configuration is assigned (cf. Werner, A., 1894, i, 461), since on warming with alcoholic potassium hydroxide they are readily hydrolysed with formation of sodium dinitrophenoxide and the corresponding nitrile: $R \cdot CH{:}N \cdot O \cdot C_6H_3(NO_2)_2 \longrightarrow RCN + (NO_2)_2C_6H_3 \cdot OH$ (cf. T., 1923, **123**, 1190). The ethers obtained from *o*-methoxy- and *p*-hydroxy-benz*anti*aldoximes behave in this way, although previously no *syn*-derivatives of these oximes had been prepared. 3-Bromo-*p*-dimethylamino- and *o*-hydroxybenz*anti*aldoximes do not react in this way, but in the former case a dinitrophenyl ether was obtained by another method. The reaction has also been studied in the case of the sodium salts of the following *syn*-oximes: benzaldoxime, *p*-methoxybenzaldoxime, cinnamaldoxime, acetaldoxime, and heptaldoxime. A complicated reaction occurs but the only products isolated were sodium dinitrophenoxide and the corresponding aldehyde. The binary fusion curves of the *anti*-oximes and chlorodinitrobenzene indicate that in certain cases, *e.g.*, benz*anti*aldoxime and *p*-methoxybenz*anti*aldoxime, well-defined additive compounds are formed containing equimolecular quantities of the two components. *o*-Methoxy- and *o*-hydroxybenz*anti*aldoximes gave no indication of such an equimolecular compound, although in the former case there is some evidence of the formation of an unstable compound of chlorodinitrobenzene (2 mols.) and oxime (1 mol.). That stable additive compounds with chlorodinitrobenzene are characteristic of those oximes which are readily converted into *syn*-isomerides affords some support for the view that the formation of additive compounds precedes isomeric change in the oximes. 2 : 4-*Dinitrophenyl ethers* were prepared from the following: p-*methoxybenz*syn*aldoxime*, m. p. 174° (decomp.); o-*aminobenz*syn*aldoxime*, m. p. 177° (decomp.); 5-*bromo*-3 : 4-*dimethoxybenz*syn*aldoxime*, m. p. 199° (decomp.); 3 : 4-*methylenedioxybenz*syn*aldoxime*, m. p. 194° (decomp.); o-*nitrobenz*syn*aldoxime*, m. p. 184° (decomp.); p-*nitrobenz*syn*aldoxime*, m. p. 210° (decomp.); p-*dimethylaminobenz*syn*aldoxime*, m. p. 185° (decomp.); 3-*nitro*-p-*dimethylaminobenz*syn*aldoxime*, m. p. 179° (decomp.); 3 : 4-*dimethoxybenz*syn*aldoxime*, m. p. 176° (decomp.); o-*methoxybenz*syn*aldoxime*, m. p. 184° (decomp.). The *mono-dinitrophenyl ether* of p-*hydroxybenz*syn*aldoxime* melts at 185° (decomp.). The 2 : 4-*dinitrophenyl ether* of 3-*bromo*-p-*dimethylaminobenz*syn*aldoxime*, m. p. 181° (decomp.), was obtained by the action of sodium hydroxide solution on the powdered fusion of the *anti*-oxime (1 mol.) with chloro-2 : 4-dinitrobenzene (1 mol.). The *additive* compound of chloro-2 : 4-dinitrobenzene with benz*anti*aldoxime has m. p. 32—33°, and with *p*-methoxybenz*anti*aldoxime, m. p. 65°.

R. B.

Secondary Valency of the Hydroxyl Group in Complex Salts of Protocatechualdehyde. H. Reihlein and A. Saffer.—(See ii, 384.)

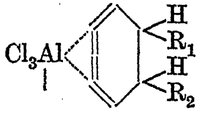
Purification and Physical Constants of Acetophenone. [illegible] L. R. Morgan and O. M. Lammert (*J. Amer. Chem. Soc.*, 1924, [illegible]).—Pure acetophenone has been prepared by a method [illegible] crystallisation in the dark and in the absence of [illegible] following constants have been determined:

freezing point 19·655°±0·002°; specific conductance k^{25} $6{\cdot}43\times10^{-9}$ mho; d_4^{25} 1·02382±0·002%. The freezing-point curve of acetophenone with small quantities of water has been determined.

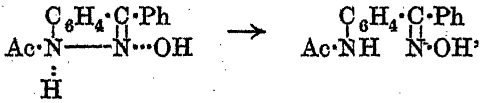
W. H.-R.

Explanation of the Catalytic Action in Friedel–Crafts' Syntheses. A. SCHAARSCHMIDT (*Z. angew. Chem.*, 1924, **37**, 286—288).—Unpublished experimental results (covered by patents) lead the author to conclude that the aluminium chloride (or ferric chloride) in a Friedel–Crafts reaction "activates" the benzene, or benzene derivative, in forming an additive compound. To the intermediate compound formed by the three reagents he ascribes the annexed formula, in which R_1 and R_2 may be alike, as in halogenation, or unlike, as in the synthesis of acetophenone. If this compound be stable, as in the acetophenone synthesis, then a molecular proportion of aluminium chloride is needed. If it be unstable, then the aluminium chloride behaves as a true catalyst. But if one of the end-products can react with the aluminium chloride then the reaction, although really catalytic, needs for completion a molecular proportion of the agent. The presence of reactive substituent groups in the benzene derivative may likewise influence the course of the reaction.

W. A. S.



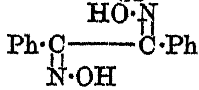
Oximes of *o*-Aminobenzophenone and the Beckmann Transformation. K. v. AUWERS and O. JORDAN (*Ber.*, 1924, **57**, [*B*], 800—808; cf. Meisenheimer and Meis, this vol., i, 433).—The configuration of the two oximes of *o*-aminobenzophenone has been deduced from their behaviour on diazotisation (A., 1893, i, 587), and is supported by the hydrolysis of 1-acetyl-3-phenylindazole with sodium hydroxide to the *N*-acetyl derivative of the *n*-oxime, m. p. 127°:



$$\begin{array}{c} C_6H_4\cdot C\cdot Ph \\ Ac\cdot N\text{———}N\cdots OH \\ \vdots \\ H \end{array} \rightarrow \begin{array}{c} C_6H_4\cdot C\cdot Ph \\ Ac\cdot NH \quad N\cdot OH \end{array}$$

m. p. 178—180°.

Both oximes are transformed by acetic acid saturated with hydrochloric acid into phenylindazole in approximately equal yields, the transformation being slightly quicker with the *h*-oxime, m. p. 156°. On boiling with acetic acid, the *n*-oxime yields exclusively its acetyl derivative, m. p. 178—180°, whereas the *h*-oxime is converted mainly into 1-acetyl-3-phenylindazole, a small quantity of the acetyl compound, m. p. 178—180°, being also formed. Both oximes on heating with alcohol at 160° in the presence of a trace of hydrochloric acid yield benzenylphenyleneamidine (2-phenylbenziminazole), m. p. 291° (A., 1891, 1378), but the *n*-oxime yields a purer product. A similar result was obtained with 4—5% formic acid at 140°, both oximes yielding a little *o*-aminobenzophenone and the iminazole, the *n*-oxime again giving the purer product. At 120°, the *h*-oxime was largely converted into *o*-aminobenzophenone, whereas the *n*-oxime gave mainly the iminazole. On boiling with concentrated formic acid, both oximes are converted into the N-*formyl* derivative of the *n*-oxime, fine needles, m. p. 165°, the *h*-oxime yielding also a small quantity of 1-formyl-3-phenylindazole. The hydrochlorides of both oximes undergo the Beckmann transformation on heating, yielding the hydrochloride of 2-phenylbenziminazole, m. p. 325—328°, the transformation being more rapid and without sintering in the case of the *n*-oxime. The N-*acetyl* derivative of the *h*-oxime, m. p. 154—155°, was obtained, together with a little of the *N*-acetate, by treating the oxime in ether–pyridine solution with acetyl chloride. The N-*benzoyl* derivative of the *h*-oxime has m. p. 175—176°, and of the *n*-oxime, m. p. 201°. Both oximes on benzoylation by the Schotten-Baumann process also yield the same *dibenzoyl* compound, m. p. 165—166°, which on hydrolysis gives only the *N*-benzoate of the *n*-oxime. Treatment with methyl sulphate converts the *N*-benzoate, m. p. 201°, into its *methyl ether*, m. p. 142—143°, but from the isomeric *N*-benzoate of m. p. 175—176° only resinous products were obtained.

The great tendency to form derivatives of the *n*-oxime and the fact that both oximes give the same diacetyl and dibenzoyl compounds contrast with the behaviour of the benzildioximes, where all three series of diacyl derivatives are known. It is suggested that the *syn*-oxime has a configuration such as  $\mathrm{Ph{\cdot}\underset{\underset{N{\cdot}OH}{\|}}{C}{-\!\!-\!\!-\!\!-}\overset{\overset{HO{\cdot}N}{\|}}{C}{\cdot}Ph}$, comparable with those suggested for the stereoisomeric substituted diphenyl derivatives (T., 1922, **121**, 614; 1923, **123**, 2047).

R. B.

Addition Reactions of Benzoylphenylacetylene. E. P. Kohler and G. R. Barrett (*J. Amer. Chem. Soc.*, 1924, **46**, 747—753).—In the presence of a little sodium methoxide in methyl-alcoholic solution, benzoylphenylacetylene and methyl cyanoacetate combine readily with the production of an intense red colour, and formation of a termolecular condensation product *methyl γ-cyano-αε-dibenzoyl-βδ-diphenyl-*$\Delta^{\alpha\delta}$*-pentadiene-γ-carboxylate*, $\mathrm{CHBz{:}CPh{\cdot}C(CN)(CO_2Me){\cdot}CPh{:}CHBz}$, yellow needles, m. p. 209°. Methyl α-cyanopropionate combines somewhat less readily with benzoylphenylacetylene. When one equivalent of sodium methoxide was used two products were obtained, *phenyl γ-cyano-β-phenylbutenyl ketone*, $\mathrm{CHMe(CN){\cdot}CPh{:}CH{\cdot}COPh}$, colourless prisms, m. p. 129°; and a yellow solid, from which a *substance* was obtained as greenish-yellow needles turning red at about 260°, m. p. 264°. The latter substance dissolved in boiling methyl alcohol gave, on evaporation of the solvent, sodium chloride and a yellow substance from which hot methyl alcohol extracted 4 : 6-*diphenyl-3-methyl*-1 : 2-*pyrone*, stout yellow needles, m. p. 113°.

In presence of a smaller quantity of the condensing agent, methyl α-cyanopropionate and benzoylphenylacetylene condense to form [illegible] *γ-cyano-δ-keto-βδ-diphenyl-α-methyl-*Δ^{β}*-pentenoate*, $\mathrm{CHBz{:}CPh{\cdot}C(CN)Me{\cdot}CO_2Me}$, [illegible] needles, m. p. 70°.

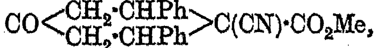
When a benzene solution of benzoylphenylacetylene was added to a suspension of the sodium derivative of benzyl cyanide, a crimson condensation *product* separated which, when decomposed with dilute hydrochloric acid, formed *phenyl γ-cyano-βγ-diphenylpropenyl ketone*, COPh·CH:CPh·CHPh·CN, colourless needles, m. p. 137°; the compound reduces permanganate in acetone, readily forms a *hydrazone*, m. p. 150—151°, and regenerates the crimson sodium compound when treated with sodium methoxide.

Equimolecular proportions of benzoylphenylacetylene and toluene-*p*-sulphinic acid, in the presence of a condensing agent, react to form *phenyl β-toluene-*p*-sulphonylstyryl ketone*,

$$COPh·CH:CPh·SO_2·C_7H_7,$$

colourless, 6-sided plates, m. p. 141°, and smaller quantities of a *stereoisomeride* (yellow needles, m. p. 157°). The yellow compound is readily obtained from its colourless stereoisomeride, when a suspension of this in methyl alcohol is treated with a trace of sodium alkoxide. Both sulphones gave, on reduction, β-toluene-*p*-sulphonyl-β-phenylpropiophenone, and a *substance* which crystallises in fine needles, m. p. 249°. C. J. S.

Addition Reactions of certain Pentadienones. E. P. Kohler and R. W. Helmkamp (*J. Amer. Chem. Soc.*, 1924, **46**, 1018—1024). —Methyl cyanoacetate combines readily with distyryl ketone and other pentadienones in presence of sodium methoxide or hydroxide to form *cyclo*hexanone derivatives. The closing of the ring takes place much more rapidly than the addition of a second molecule of cyanoacetate. No open-chain compounds are formed as is the case with malonic and acetoacetic esters. The products do not reduce permanganate. They are extracted from ethereal solution by sodium hydrogen sulphite, and form acetals with surprising ease. The *cyclo*hexanones occur in two stereoisomeric forms; that first formed is transformed into a second, more stable to alkali, by treatment with sodium hydroxide. *Methyl 1-cyano-4-keto-2 : 6-diphenyl*cyclo*hexane-1-carboxylate*,



$$CO{<}{\begin{matrix}CH_2·CHPh\\CH_2·CHPh\end{matrix}}{>}C(CN)·CO_2Me,$$

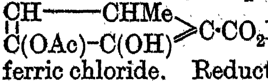
white filaments, m. p. 137—138°, is obtained on adding a few drops of a sodium methoxide solution to a hot saturated solution of distyryl ketone in methyl alcohol containing a little more than one equivalent of methyl cyanoacetate. Using aqueous sodium hydroxide, the isomeride is obtained in stout prisms, m. p. 146°; *oxime*, m. p. 190°; *methyl acetal*, by passing dry hydrogen chloride into a solution of the *cyclo*hexanone derivative in dry, cooled methyl alcohol, m. p. 181°. The *ethyl acetal*, m. p. 151—152°, was made as above and also by the Claisen method. The melting point may drop as low as 135—145° after standing some hours, but after one recrystallisation it is again 151—152°. Bromination gave a product containing 1—2% more bromine than required for a dibromo derivative. *1-Cyano-4-keto-2 : 6-diphenyl*cyclo*hexane-1-carboxylic acid* forms needles or large, colourless prisms containing 1 mol. of acetone. On heating at 180—190°, the acetone is driven off, followed by a mol. of carbon dioxide, giving 4-*cyano*-3 : 5-*diphenyl*cyclo*hexan*-1-*one*, minute prisms, m. p. 81—83° (decomp.); *semicarbazone*, minute prisms, m. p. 194—196° (decomp.). *Methyl* 4-*keto*-2 : 6-*diphenyl*cyclo*hexane*-1-*carboxylate*, prisms, m. p. 104·5—106°, is formed by heating the above nitrile in methyl-alcoholic hydrochloric acid. Dimethoxystyryl ketone reacts with methyl cyanoacetate in presence of a little sodium methoxide at room temperature to give a mixture of stereoisomerides of which the m. p. varies with the solvent used for crystallisation. *Methyl* 1-*cyano*-4-*keto*-2 : 6-*dianisyl*cyclo*hexane*-1-*carboxylate* is obtained as the more stable isomeride on boiling with sodium methoxide, needles, m. p. 208—209°; *methyl acetal*, m. p. 175·5—176°. Ethyl cyanoacetate condenses similarly with dimethoxystyryl ketone, and the condensation product gave the *ethyl acetal* of the above, m. p. 132—134°. A. C.

Addition Reactions of certain Pentadienones. II. Addition of Malonic Esters. E. P. Kohler and C. S. Dewey (*J. Amer. Chem. Soc.*, 1924, **46**, 1267—1278).—The condensation of methyl malonate with distyryl ketone in presence of bases leads to an equilibrium mixture of the three products $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH(CO_2Me)_2$ (I), $CO[CH_2{\cdot}CHPh{\cdot}CH(CO_2Me)_2]_2$ (II), and *dimethyl* 4-*keto*-2 : 6-*diphenyl*cyclo*hexane*-1 : 1-*dicarboxylate* (III), from which either may be isolated by inoculation or suitable variation of conditions. Compound (III), produced in presence of sodium methoxide, forms white, irregular prisms, m. p. 135°, from which the free *acid*, $C_{20}H_{18}O_5,2H_2O$, is obtained on hydrolysis as transparent needles. The latter is stable in a vacuum, but becomes anhydrous at 75—100°, and melts at about 150° with loss of carbon dioxide and formation of the corresponding monocarboxylic acid. *Diethyl* 4-*keto*-2 : 6-*diphenyl*cyclo*hexane*-1 : 1-*dicarboxylate* forms white needles, m. p. 79°. *Dimethyl* δ-*keto*-βζ-*diphenyl*-Δ -*hexene*-αα-*dicarboxylate* (I), long, silky needles, m. p. 108°, is obtained in presence of piperidine. On oxidation with cold permanganate in acetone, it yields benzoic acid and the monomethyl ester of a tribasic acid, $C_{13}H_{14}O_6$, colourless prisms, m. p. 101°, which, by hydrolysis with potassium hydroxide and subsequent heating at 170—185°, yields carbon dioxide and phenylglutaric acid, m. p. 136°. (I) is converted quantitatively into (III) by adding it to a cold solution of sodium methoxide (5%) in methyl alcohol, but in presence of methyl malonate the compound (II) was obtained as long, silky needles, m. p. 109—112°. *Dimethyl* δ-*keto*-βζ-*diphenylhexane*-αα-*dicarboxylate*, $CH_2Ph{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH(CO_2Me)_2$, m. p. 57°, is obtained by the condensation of methyl malonate with phenylethyl styryl ketone in presence of sodium methoxide. Methyl cyanoacetate condenses with distyryl ketone to form a cyclohexanone derivative much more rapidly than methyl malonate. [illegible] *diphenyl*cyclo*hexan*-1-*one*, obtained by the condensation of [illegible] ketone and nitromethane, forms colourless, [illegible] m. p. 93—94°. It forms a *sodium* derivative.

from which 4-*bromo*-4-*nitro*-3 : 5-*diphenyl*cyclo*hexan*-1-*one*, small prisms, m. p. 156—157°, is obtained by the action of bromine. Styryl *p*-methoxystyryl ketone and dimethyl malonate yield a *cyclo*hexanone derivative, fine, white needles, m. p. 145—146° analogous with (III), in presence of sodium methoxide. In presence of piperidine, *dimethyl δ-keto-β-phenyl-ζ-*p-*anisyl-Δ^{ϵ}-hexene-αα-dicarboxylate*, white needles, m. p. 124°, is also obtained. Styryl δ-phenylbutadienyl ketone yields similarly the *cyclo*hexanone *derivative*, $C_{24}H_{24}O_5$, lustrous, transparent prisms, m. p. 156°, and the *compound* CHPh:CH·CH:CH·CO·CH_2·CHPh·CH(CO_2Me)$_2$, white needles, m. p. 112°, which is very readily converted into the cyclic compound. Di-*p*-methoxystyryl ketone and methyl malonate yield the *cyclo*hexanone derivative, $C_{24}H_{26}O_7$, brilliant prisms, m. p. 194°, but the open-chain compound could not be isolated. *p*-Methoxystyryl δ-phenylbutadienyl ketone and di-δ-phenylbutadienyl ketone behave similarly, with formation, respectively, of *dimethyl* 4-*keto*-2-*anisyl*-6-*styryl*cyclo*hexane*-1 : 1-*dicarboxylate*, lustrous tables or prisms, m. p. 170°, and *dimethyl* 4-*keto*-2 : 6-*distyryl*cyclo*hexane*-1 : 1-*dicarboxylate*, small, lustrous prisms, m. p. 112°.

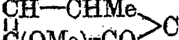
F. G. W.

Insecticides. VI. *cyclo*Pentanolone Derivatives and their Comparison with Pyrethrolone. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 377—390).—A number of simpler *cyclo*pentanolone derivatives have been prepared by condensing ethyl glutarate or β-methylglutarate with ethyl oxalate (Dieckmann, A., 1894, i, 324). The properties of the compounds obtained are similar in most respects to those of pyrethrolone and its derivatives (this vol., i, 523). From ethyl glutarate and ethyl oxalate, ethyl $\Delta^{2:4}$-*cyclo*pentadiene-3 : 4-diol-2 : 5-dicarboxylate is obtained which, by hydrolysis with 20% sulphuric acid, gives Δ^2-*cyclo*penten-3-ol-4-one, but with more dilute acid gives *ethyl*-Δ^2-cyclo*penten*-3-*ol*-4-*one*-2-*carboxylate*, m. p. 103°, b. p. 120°/1 mm. By reduction with hydrogen and palladium, the *cyclo*pentenolone gives cyclo*pentan*-3-*ol*-4-*one*, b. p. 77—78°/10 mm., which slowly forms a polymeride, m. p. 88—90°. Ethyl 1-methyl-$\Delta^{2:4}$-*cyclo*pentadiene-3 : 4-diol-2 : 5-dicarboxylate, m. p. 110° (cf. Dieckmann, A., 1899, i, 676), is hydrolysed by 10% sulphuric acid to *ethyl* 1-*methyl*-Δ^2-cyclo*penten*-3-*ol*-4-*one*-2-*carboxylate*, a pale yellow liquid, b. p. 103—107°/0·5 mm.; the *acetate*, a colourless oil, b. p. 95°/0·1 mm., probably has the structure



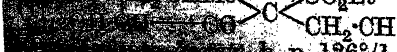
$$\left.\begin{matrix}\mathrm{CH}\text{——}\mathrm{CHMe}\\ \| \\ \mathrm{C(OAc)}\text{-}\mathrm{C(OH)}\end{matrix}\right\rangle \mathrm{C{\cdot}CO_2Et}$$

since it gives a strong reaction with ferric chloride. Reduction of the ester with hydrogen and palladium does not proceed smoothly, but some *ethyl* 1-*methyl*cyclo*pentan*-3-*ol*-4-*one*-2-*carboxylate* is obtained, a colourless oil, b. p. 104—105°/0·25 mm. (*acetate*, b. p. 104—105°/0·2 mm.), together with some 1-methyl*cyclo*pentanone. Hydrolysis of the last ester with 20% sulphuric acid gives not the expected methyl*cyclo*pentanolone, but 1-*methyl*-Δ^2-cyclo*penten*-4-*one*, colourless liquid, b. p. 57—59°/11 mm.; *semicarbazone*, m. p. 223°; p-*nitrophenylhydrazone*,

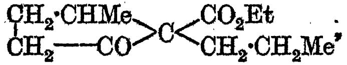
m. p. 175—176°. The *ethyl ether* of the above ester is obtained by prolonged action of boiling alcoholic sulphuric acid on the ester; it forms a colourless oil, b. p. 82—83°/0·5 mm. 1-*Methyl*-Δ^2-cyclo*penten*-3-*ol*-4-*one* (or 1-*methyl*cyclo*pentane*-3 : 4-*dione*) is obtained by hydrolysis of the above dicarboxylate with 20% sulphuric acid; it forms yellow crystals, m. p. 58—59°, b. p. 105°/21 mm., and has an odour similar to that of cresol. With *p*-nitrophenylhydrazine, it forms an *osazone*, m. p. 180°, and also gives a *benzoate*, $C_{13}H_{12}O_3$, a viscous oil, b. p. 138—140°/0·2 mm., and an *acetate*, $C_8H_{10}O_3$, b. p. 128—130°/12 mm. The *methyl ether*,  $\begin{matrix}\text{CH—CHMe}\\ \Vert\\ \text{C(OMe)·CO}\end{matrix}\!\!>\!CH_2$, is a colourless oil, b. p. 105—106°/15 mm. (*semicarbazone*, m. p. 192°), and the *ethyl ether* has b. p. 112—113°/10 mm. When the ethyl ether is heated at 200° with pyridine or quinoline, the ethyl group wanders from the oxygen to a carbon atom, forming a 1-*methyl*-2(5)-*ethyl*-Δ^2-cyclo*penten*-3-*ol*-4-*one*, a pale yellow oil, b. p. 112°/10 mm. 1-*Methyl*cyclo*pentan*-3-*ol*-4-*one*, obtained by reduction of the corresponding *cyclo*pentene derivative, is a colourless oil, b. p. 86°/12 mm.; it has powerful reducing properties and by auto-oxidation forms the *cyclo*pentenolone. With chrysanthemumic acid, it forms a non-insecticidal ester. The p-*nitrophenylhydrazone* has m. p. 215—216°, and the *methyl ether* is a colourless oil, b. p. 171—172°/14 mm. 1-Methyl*cyclo*pentan-3-ol-4-one forms a *polymeride*, m. p. 85—86°, which reverts on distillation to the liquid modification. 1-*Methyl*-3-*ethoxy*cyclo*pentan*-4-*one*, colourless liquid, b. p. 83—85°/12 mm., is obtained by reduction (Paal–Skita) of the corresponding methylethoxy*cyclo*pentenone. The *acetate* of 1-methyl*cyclo*pentan-3-ol-4-one is a colourless oil, b. p. 109°/14 mm. (*semicarbazone*, m. p. 174°; p-*nitrophenylhydrazone*, m. p. 163°), and the *benzoate* has m. p. 55—56°.

E. H. R.

Insecticides. VIII. Preparation of Alcohols Similar to Pyrethrolone. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 406—441).—Experiments were made to determine whether the unsaturated side-chain of pyrethrolone (1-methyl-2-pentadienyl*cyclo*pentan-4-ol-3-one, this vol., i, 523) can be replaced by other unsaturated groups without destroying the insecticidal properties of its chrysanthemumic acid ester. Methylallyl*cyclo*pentanolone (IV below) forms an insecticidal ester, weaker, however, than pyrethrine.

By the action of allyl bromide on the sodium derivative of ethyl 4-acetoxy-1-methyl*cyclo*pentan-3-one-2-carboxylate, and removal of the acetyl group with cold concentrated hydrochloric acid, was obtained *ethyl* 1-*methyl*-2-*allyl*cyclo*pentan*-4-*ol*-3-*one*-2-*carboxylate*  $\begin{matrix}\text{CH}_2\text{·CHMe}\\ \text{[illegible]——CO}\end{matrix}\!\!>\!C\!<\!\begin{matrix}CO_2Et\\ CH_2\text{·}CH\text{:}CH_2\end{matrix}$, a viscous, colourless oil, b. p. [illegible] b. p. 126°/1 mm. The ester is extraordinarily [illegible] action of barium hydroxide it is converted [illegible] methyl-Δ^{δ}-*octenoic acid*,

$\mathrm{CH_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CHMe{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H}$ (II), the *lactone* of which forms a viscous mass, b. p. 165° in a high vacuum. The *chrysanthemumcarboxylate* of (I) is a viscous oil, b. p. 180° in a vacuum, and is non-insecticidal. Reduction of the acetate of (I) by the Paal–Skita method gives *ethyl 4-acetoxy-1-methyl-2-propyl*cyclo*pentan-3-one-2-carboxylate*, b. p. 127°/1 mm., which is further reduced by aluminium amalgam in ether solution to *ethyl 1-methyl-2-propyl*cyclo*pentan-3-one-2-carboxylate*,

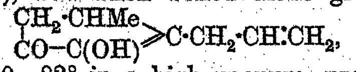


$$\begin{matrix}\mathrm{CH_2{\cdot}CHMe}\\ \mathrm{CH_2{-}{-}CO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CO_2Et}\\ \mathrm{CH_2{\cdot}CH_2Me}\end{matrix},$$

b. p. 134—136°/11 mm. (*semicarbazone*, m. p. 183°). Reduction of this with hydrogen iodide gives *1-methyl-2-propyl*cyclo*pentan-3-one*; *semicarbazone*, m. p. 173—174°. The *ethyl ether* of (I), obtained by the action of allyl bromide on the sodium derivative of ethyl 4-ethoxy-1-methyl*cyclo*pentan-3-one-2-carboxylate, is a colourless oil, b. p. 96°/0·1 mm. The ether resists the action of acids, and by alkalis is converted into the *ethyl ether* of (II), b. p. 155—160° in a high vacuum.

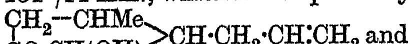
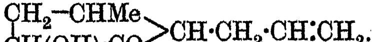
Ethyl 1-methyl-Δ^4-*cyclo*penten-4-ol-3-one-2-carboxylate, in the form of its sodium or silver salt, reacts slowly with allyl bromide, forming an *O-allyl ether*, a pale yellow oil, b. p. 105°/0·5 mm., which when heated with pyridine isomerises into *ethyl 1-methyl-2-allyl-Δ^4-*cyclo*penten-4-ol-3-one-2-carboxylate*, b. p. 120°/0·9 mm.; by acid hydrolysis this gives *1-methyl-2-propenyl-Δ^4-*cyclo*penten-4-ol-3-one* (III), m. p. 110°. The same compound is obtained by the action of allyl bromide on ethyl 1-methyl-$\Delta^{2:4}$-*cyclo*pentadiene-3 : 4-diol-2 : 5-dicarboxylate, followed by decomposition of the condensation product with acid or alkali. The compound is very sensitive to atmospheric oxidation. Its *chrysanthemumcarboxylate*, a viscous oil, b. p. 165°/1 mm., is non-insecticidal. The presence of the propenyl group is proved from the formation of acetaldehyde by the decomposition of the ozonide; allyl derivatives give formaldehyde. Reduction of (III) with hyposulphite or electrolytically gives *1-methyl-2-propyl-$\Delta^{2(4)}$-*cyclo*penten-3(4)-ol-4(3)-one*, crystals, m. p. 46—48°, which by further reduction gives the corresponding *cyclo*pentanolone. With bromine, (III) forms a *dibromide*, white crystals, m. p. 100—102°. Attempts to prepare a methylpropenyl*cyclo*pentanolone by reduction of the *acetate* (b. p. 108°/0·5 mm.) and *methyl ether* (colourless oil, b. p. 127—128°/12 mm.) of (III) were unsuccessful.

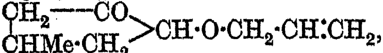
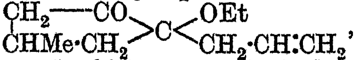
By the action of allyl bromide in presence of sulphuric acid on 1-methyl-Δ^2-*cyclo*penten-3-ol-4-one, the *allyl ether* of the last is obtained, a mobile oil, b. p. 76—77°/0·75 mm., which by the action of alkalis is converted into the 2-propenyl compound, m. p. 110° (III, above), but when boiled alone gives *1-methyl-2-allyl*cyclo*pentenolone*,



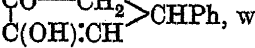
$$\begin{matrix}\mathrm{CH_2{\cdot}CHMe}\\ \mathrm{CO{-}C(OH)}\end{matrix}\!>\!\mathrm{C{\cdot}CH_2{\cdot}CH{:}CH_2},$$

a pale yellow, mobile oil, b. p. 80—82° in a high vacuum, probably a mixture of the Δ^2- and Δ^4-isomerides. By reduction with zinc and acetic acid, this gives *1-methyl-2-allyl*cyclo*pentanolone* (IV), an oil, b. p. 132

134°/14 mm., which is also probably a mixture of the two isomerides,  $\begin{matrix}CH_2\text{—}CHMe\\ CO\cdot CH(OH)\end{matrix}>CH\cdot CH_2\cdot CH{:}CH_2$ and  $\begin{matrix}CH_2\text{—}CHMe\\ CH(OH)\cdot CO\end{matrix}>CH\cdot CH_2\cdot CH{:}CH_2$. Its *chrysanthemumcarboxylate*, b. p. 150°/1 mm., has insecticidal properties.

The sodium derivative of 1-methyl*cyclo*pentanolone reacts with allyl bromide to form the *allyl ether*,  $\begin{matrix}CH_2\text{——}CO\\ CHMe\cdot CH_2\end{matrix}>CH\cdot O\cdot CH_2\cdot CH{:}CH_2$, a colourless oil, b. p. 112°/12 mm. On the other hand, the ethyl ether, when treated with sodium and allyl bromide in ether solution, gives 3-*ethoxy*-1-*methyl*-3-*allyl*cyclo*pentan*-4-*one*,

$\begin{matrix}CH_2\text{——}CO\\ CHMe\cdot CH_2\end{matrix}>C<\begin{matrix}OEt\\ CH_2\cdot CH{:}CH_2\end{matrix}$,
a colourless oil, b. p. 110°/13 mm., which, by boiling with 20% sulphuric acid, gives 1-*methyl*-3-*allyl*-Δ^2-cyclo*penten*-4-*one*, a pale yellow oil, b. p. 112—115°/17 mm. (*semicarbazone*, crystals, decomp. 215°). When this is reduced by the Paal–Skita method, it gives 1-*methyl*-3-*propyl*cyclo*pentan*-4-*one*, a colourless oil, b. p. 82—83°/10 mm., having a faint odour of menthone; *semicarbazone*, m. p. 183°. This compound was synthesised by the action of propyl iodide on ethyl methyl*cyclo*pentanonecarboxylate prepared from ethyl β-methyladipate. Its *chrysanthemumcarboxylate*, an oil, b. p. 140—142°/0·7 mm., is not insecticidal.

Attempts to prepare methyl*cyclo*pentanolone derivatives with a geranyl side-chain were unsuccessful. 1-*Methyl*-Δ^2-cyclo*penten*-3-*ol*-4-*one geranyl ether* is a pale yellow oil, b. p. 138—142°/0·75 mm.; under no conditions does the geranyl group pass from oxygen to carbon. The *benzylidene* derivative of 1-methyl*cyclo*pentanolone is a viscous oil, b. p. 140°/1 mm. E. H. R.

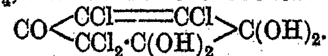
Insecticides. IX. Preparation of *cyclo*Pentanolon Derivatives with Unsaturated Side Chains. H. STAUDINGER and L. RUZICKA (*Helv. Chim. Acta*, 1924, 7, 442—448).—Continuing the search for substitutes for pyrethrolone (preceding abstract), a number of substituted *cyclo*pentanolones have been prepared, none of which, however, gave insecticidal esters with chrysanthemumcarboxylic acid. By boiling ethyl 1-phenyl-3 : 4-dihydroxy*cyclo*pentadiene-2 : 5-dicarboxylate with 10% sulphuric acid, 1-*phenyl*cyclo*pentenolone*,  $\begin{matrix}CO\text{——}CH_2\\ C(OH){:}CH\end{matrix}>CHPh$, was obtained, white crystals, m. p. 103—105°, which by reduction gave the corresponding 1-*phenyl*cyclo*pentanolone* in an impure form. *Methyl* 1-*styryl*-3 : 4-*dihydroxy*cyclo*pentadiene*-2 : 5-*dicarboxylate*, crystals, m. p. 141—142°, was obtained by condensing methyl β-styrylglutarate [illegible] ethyl oxalate. By boiling 20% sulphuric acid, it is converted [illegible]-Δ^2-cyclo*penten*-3-*ol*-4-*one*, colourless crystals, m. p. [illegible] reduced by zinc in sulphuric acid to 1-*styryl*-[illegible] colourless crystals, m. p. 48—50°.

[illegible] condenses with ethyl malonate to give, not the [illegible] but *ethyl* β-*methyl*-Δ^γ-*pentene*-$\alpha\alpha\epsilon\epsilon$-

tetracarboxylate, a viscous oil, b. p. 174—175°/0·5 mm.; *methyl* ester, b. p. 134°/12 mm.

Ethyl *cyclo*pentan-2-one-1-carboxylate in the form of its sodium derivative condenses with allyl bromide to give *ethyl* 1-*allyl*cyclo*pentan*-2-*one*-1-*carboxylate*, a colourless oil, b. p. 125°/11 mm., which is converted by boiling 20% sulphuric acid into 1-*allyl*-cyclo*pentan*-2-*one*, a colourless oil, b. p. 86°/12 mm. (p-*nitrophenylhydrazone*, yellow crystals, m. p. 139°), which when heated with amyl formate gives a 3-*hydroxymethylene* derivative, mobile oil, b. p. 117°/11 mm. With magnesium methyl iodide, allyl*cyclo*pentanone gives 1-*methyl*-2-*allyl*cyclo*pentan*-1-*ol*, a colourless oil, b. p. 85°/13 mm. E. H. R.

***iso*Nitriles. VII. Interaction of Phenylcarbylamine and β-Naphthol.** M. Passerini (*Gazzetta*, 1924, **54**, 184—191).—A fuller account of work already published (this vol., i, 57). The dianil derivative of 2-hydroxy-1-naphthylglyoxal has the normal molecular weight in freezing benzene; its *benzoyl* derivative, $C_{31}H_{22}O_2N_2$, forms minute, pink crystals, m. p. 163—165°, and reddens rapidly in the air. 2-Hydroxy-1-naphthylglyoxal diphenylhydrazone, $OH\cdot C_{10}H_6\cdot C(:N\cdot NHPh)\cdot CH:N\cdot NHPh$, has m. p. 240° (decomp.). The *lactone* of 2-*hydroxy*-1-*naphthylglyoxylic acid* (*loc. cit.*), forms yellow needles, m. p. 184—185°, has an acid reaction towards indicators, and gives an intense red coloration with concentrated sulphuric acid. The *barium* salt of the corresponding acid has been prepared. T. H. P.

3 : 3 : 5 : 6-Tetrachloro- and -Tetrabromo-1 : 2 : 4-triketo-*cyclo*hexenes. T. Zincke and E. Weishaupt (*Annalen*, 1924, **437**, 86—105).—The two compounds, $C_6H_4O_8N_2Cl_4$ and $C_6H_4O_5Cl_4$, obtained from tetrachloro-*o*-benzoquinone (Zincke, this vol., i, 163) have now been prepared by treating tetrachloropyrocatechol with fuming nitric acid containing 10% of sulphuric acid. Tetrabromopyrocatechol yields analogous compounds. The compound, $C_6H_4O_5Cl_4$, is shown to be 3 : 3 : 5 : 6-*tetrachloro*-1 : 2 : 4-*triketo*cyclo*hexene dihydrate*,  $CO<\begin{smallmatrix}CCl{=\!=}CCl\\CCl_2\cdot C(OH)_2\end{smallmatrix}>C(OH)_2$. It is also obtained by chlorinating (and simultaneously hydrolysing) triacetylhydroxyquinol and forms pale yellow needles, m. p. 96°. When reduced it yields 3 : 5 : 6-trichloro-1 : 2 : 4-trihydroxybenzene (Zincke and Schaum, A., 1894, i, 231) and when heated at 120—125°, or with water or dilute acid decomposes giving trichlorohydroxybenzoquinone (Zincke and Schaum, *loc. cit.*) and a compound, $C_5O_2Cl_4$, probably 1 : 2 : 4 : 4-*tetrachloro*-3 : 5-*diketo*cyclo*pentene*. The latter was the sole product when the triketo compound was treated with calcium hypobromite. It is a steam-volatile substance with a quinone-like odour, forming broad needles, m. p. 65°, giving an *anilide*, $C_5O_2Cl_3\cdot NHPh$, yellow needles, m. p. 165°, and with *o*-phenylenediamine a *eurhodol*, $C_5(OH)Cl_3:N_2C_6H_4$, yellow needles, strongly fluorescent in alcoholic solution. Similarly, 3 : 3 : 5 : 6-*tetrabromo*-1 : 2 : 4-*triketo*cyclo*hexene*, pale yellow prisms or tables, m. p. 83—84°, was obtained (together with the compound $C_6H_4O_8N_2Br_4$)

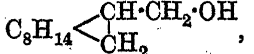
by treating tetrabromopyrocatechol with the mixed acid. When reduced, it gives 3 : 5 : 6-tribromo-1 : 2 : 4-trihydroxybenzene (Thiele and Jaeger, A., 1901, i, 701), and decomposes like the chloro-compound but more readily, yielding tribromohydroxybenzoquinone, and 1 : 2 : 4 : *4-tetrabromo*-3 : *5-diketo*cyclo*pentene*, pale yellow prisms, m. p. 142—143°; *anilide*, yellow needles, m. p. 182°; *eurhodol*, yellow needles, darkening but not melting at 170° and giving a strongly fluorescent solution. This diketone treated with sodium hypobromite gives bromoform and dibromomaleic acid (cf. Pfeiffer and Böttler, A., 1919, i, 62); with 80% alcohol at 100° it is converted into 2 : 4 : *4-tribromo*-3 : *5-diketo*cyclo*pentenol*, a crystalline powder, m. p. 196° (decomp.), reconverted into the parent substance by phosphorus pentabromide; the corresponding *methoxy* (leaflets, m. p. 89—90°) and *ethoxy* (pale yellow needles, m. p. 111—112°) compounds are obtained when anhydrous alcohols are used and are hydrolysed to the hydroxy derivative by heating with dilute alcohol. W. A. S.

Studies in the Anthracene Series. VIII. E. de B. Barnett and M. A. Matthews (*J. Chem. Soc.*, 1924, **125**, 1079—1083; cf. Battegay, A., 1923, i, 1103, 1104).—The anthraquinonesulphonic acids on reduction with iron and hydrochloric acid are readily converted into the corresponding anthronesulphonic acids, from which the dianthronesulphonic acids are obtained by oxidation with sodium peroxide. The following *sodium* and *aniline anthrone-* and *dianthrone-sulphonates* are described: 9-(or 10-)anthrone-1-sulphonate; -2-sulphonate; -1 : 5-disulphonate; and -1 : 8-disulphonate; dianthrone-ββ′-disulphonate, -1 : 5 : 1′ : 5′-tetrasulphonate, and -αα α′α′-tetrasulphonate. The aniline salts have no definite melting points (cf. A., 1923, i, 234). The change of colour of the anthrone-1 : 8-disulphonic acid on the addition of alkali is sufficiently sharp for use as an indicator. On reduction with aqueous sodium sulphide, the anthraquinonesulphonic acids are reduced to the corresponding anthraquinolsulphonic acids and in consequence act as catalysts in reduction reactions with sodium sulphide. The additive compounds of the anthracenemonosulphonic acids with nitric acid are too unstable to be isolated, but on treatment with pyridine are converted into the corresponding nitroanthracenesulphonic acids. 9-(or 10-)*Nitroanthracene*-1-*sulphonic acid*, yellow needles, and 9-(or 10-)*nitroanthracene-2-sulphonic acid* were prepared, but no nitro compound could be obtained from anthracene-1 : 5- or -1 : 8-disulphonic acid. Anthracene-2-sulphonic acid does not give an aniline salt under the usual conditions, but the following well crystallised salts were prepared: *aniline anthracene*-1-*sulphonate*, *aniline anthracene*-1 : 5-*disulphonate*, *aniline anthracene*-1 : 8-*disulphonate*. R. B.

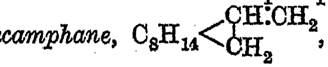
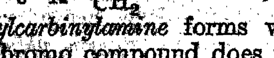
[illegible]hydroxymethylanthraquinones. III. Synthesis of [illegible] A. Jacobson and R. Adams (*J. Amer. Chem. Soc.*, [illegible]—3 : 5-Dimethoxy-2-(2′-hydroxy-4′-methyl- [illegible] treated with bromine in glacial acetic [illegible]-*bromo* derivative, thick, white needles,

m. p. 258—259°. On heating with fuming sulphuric acid and boric acid and diluting, 4-*bromo*-1-*hydroxy*-6 : 8-*dimethoxy*-3-*methylanthraquinone*, orange-red needles, m. p. 208—209°, was obtained. This yielded 1 : 6 : 8-trihydroxy-3-methylanthranol (emodin anthranol) on reduction with hydriodic acid in glacial acetic acid, from which 1 : 6 : 8-trihydroxy-3-methylanthraquinone, identical with natural emodin, was obtained on oxidation with chromic oxide in glacial acetic acid. F. G. W.

Camphanylcarbinol. H. Rupe and J. Brin (*Helv. Chim. Acta*, 1924, 7, 546—556).—Bornylenecarboxylic acid was obtained by heating borneolcarboxylic acid with acetic anhydride (cf. Bredt, A., 1909, i, 499). The *chloride* has b. p. 110°/11 mm.; *ethyl* ester, b. p. 114—115°/10 mm.; *phenyl* ester, rhombic crystals, m. p. 63—64°. By electrolytic reduction of the potassium salt, camphanecarboxylic acid was obtained; *chloride*, b. p. 110°/12 mm.; *ethyl* ester, b. p. 113°/11 mm.; *phenyl* ester, long prisms, m. p. 41°. *Camphanylcarbinol* (*hydroxymethylcamphane*),



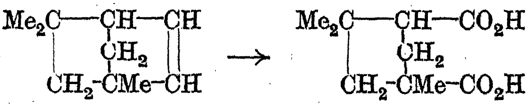
$$C_8H_{14}<\begin{matrix}CH{\cdot}CH_2{\cdot}OH\\|\\CH_2\end{matrix},$$

is obtained by reduction of the esters of either of the above acids with sodium and alcohol, the best yield, 65—70% of theory, being obtained from ethyl camphanecarboxylate. It has b. p. 117—118°/11 mm., m. p. 28°, is readily volatile in steam, and has a characteristic, sweet odour. It forms a crystalline compound with calcium chloride, which serves for its purification. The *formate* is a mobile liquid, b. p. 110°/11 mm.; *acetate*, b. p. 120°/11 mm.; *benzoate*, b. p. 195°/12 mm.; p-*nitrobenzoate*, long, white needles, m. p. 99—100°; p-*aminobenzoate*, glistening leaflets. The carbinol is dehydrated much less readily than camphylcarbinol (A., 1919, i, 29), but when heated with phosphoric acid is converted into *methylenecamphane*,  $C_8H_{14}<\begin{matrix}CH{:}CH_2\\|\\CH_2\end{matrix}$, a mobile oil with a strong, unpleasant odour, b. p. 58—62°/11 mm. The constitution of this compound is proved by the formation from it of *bromomethylcamphane*, b. p. 105—108°/12 mm., d_4^{20} 1·1948, $[\alpha]_D^{20}$ 11·57°, which is also obtained by the action of hydrogen bromide and acetic acid on the carbinol. The bromo compound reacts with aniline to give *phenylcamphanylcarbinylamine*,  $C_8H_{14}<\begin{matrix}CH{\cdot}CH_2{\cdot}NHPh\\|\\CH_2\end{matrix}$, b. p. 190—193°/11 mm.; p-*tolylcamphanylcarbinylamine* forms white, silky needles, m. p. 61—62°. The bromo compound does not form a compound with magnesium, but is converted into *dicamphanylethane*, a viscous oil, b. p. 205—208°/11 mm. E. H. R.

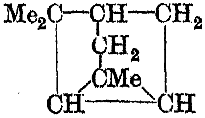
The Rotation Dispersion of Camphor. F. Bürki (*Helv. Chim. Acta*, 1924, 7, 537—540).—Measurements of the rotation dispersion of camphor made by Rupe (A., 1915, ii, 717) and Gumprich (*Physikal. Z.*, 1923, **24**, 434) are compared by calculating Rupe's characteristic wave-length, λ_a, the λ_0 of Lowry and Dickson, and Rupe's product, $\lambda_0 . \lambda_a$. The rotation-dispersion in benzene is slightly anomalous, and it is recommended to use alcohol when possible for such measurements. E. H. R.

Probable Presence of Thujone in the Essential Oil of *Artemisia Herba Alba*. E. Alinari (*Annali Chim. Appl.*, 1924, **14**, 109—112).—This oil, d^{15} 0·9257, α_D^{18} +3·88°, n_D^{20} 1·4653, contains 14·4% of free, and 7·39% of combined alcohols, calculated as $C_{10}H_8O$. The presence of camphor has been demonstrated and that of thujone is probable (cf. Grimal, A., 1904, ii, 605; also *B.*, 1924, 536). T. H. P.

The Xanthate Method in the Fenchone and *iso*Fenchone Series. S. Nametkin (*J. pr. Chem.*, 1923, ii, **106**, 25—38).—Assuming Semmler's formulæ for fenchone and *iso*fenchone, the elimination of water in the normal (1 : 2) position is only possible with *iso*fenchyl alcohol, and the hydrocarbon obtained should be analogous to bornylene. This is substantiated by the fact that fenchylene (I), obtained by the decomposition of *iso*fenchyl xanthate, on oxidation with potassium permanganate is converted into fenchocamphoric acid (II).

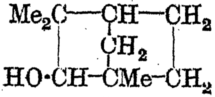


(I.) (II.)

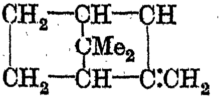


(III.)

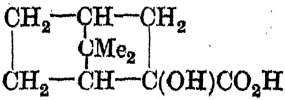
The dehydration of *iso*fenchyl alcohol takes place also in the 1 : 3 position, leading to the formation of the isomeric *cyclo*fenchene (III). On the other hand, fenchyl alcohol (IV) cannot eliminate the elements of water in the 1 : 2 position and, as might be expected, by dehydration gives the same *cyclo*fenchene. dl-*Fenchene* (V) is also produced in the reaction, giving *dl*-hydroxyfenchenic acid (VI) by oxidation with potassium permanganate.



(IV.)



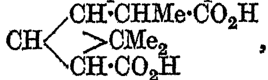
(V.)



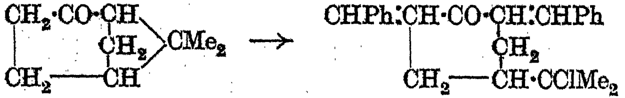
(VI.)

[With A. Selivanov.]—*dl*-Fenchene was prepared by the dehydration of crude fenchyl alcohol with phthalic acid. The fraction, b. p. 194—199°, heated with phthalic anhydride at 170°, forms a crystalline *hydrogen phthalate* which was converted into *sodium fenchyl phthalate*, m. p. 146·5°, $[\alpha]_D$ +23·23°. On hydrolysis with alcoholic potassium hydroxide it yields pure fenchyl alcohol, b. p. 200—200·5°/750 mm., m. p. 49°, $[\alpha]_D$ −10·9°. Its steric configuration corresponds with that of borneol as shown by its stability towards the dehydrating action of phthalic acid. The stereoisomeride corresponding with *iso*borneol is probably liquid and, on account of its ready elimination of water, cannot be present in the crystalline alcohol. *cyclo*Fenchene, $C_{10}H_{16}$, is obtained by heating ethyl fenchylxanthate at 150—170°, finally raising the temperature to 230°. The crude product was left with 1½% potassium permanganate solution for some time, the excess of oxidant removed, and the hydrocarbon distilled three times over sodium. It was identical with Aschan's *cyclo*fenchene (β-pinolene); b. p. 143—143·5°/747·5 mm., d_4^{20} 0·8609, n_D^{20} 1·4532, $[\alpha]_D$ −1·77° (cf. A., 1912, i, 198). The hydration of *cyclo*fenchene yields a product which on oxidation is converted into *cis*-fenchocamphoric acid and would thus seem to be *iso*fenchyl alcohol, since oxidation of this alcohol has been shown to give the same product. An oily product unattacked by permanganate is also found among the products of hydration. The oxidation product obtained from the crude fenchenes by potassium permanganate contains *dl*-hydroxyfenchenic acid, m. p. 154—155°, $[\alpha]_D$ −37·42° in ether, proving definitely the presence of the *dl*-fenchene in the crude fenchene.

[With A. Ruschentzeff.]—Crude *iso*fenchyl alcohol is obtained by hydration of *dl*-fenchene. It was purified by conversion into the xanthate from which, by the action of alcoholic ammonia, the *xanthamide* was obtained, needles, m. p. 69—70°, $[\alpha]_D$ −37·77° in alcohol. Hydrolysis of the amide by alcoholic alkali gives pure *iso*fenchyl alcohol, m. p. 60·5—61°, $[\alpha]_D$ −27·04° in alcohol. Fenchylene is obtained by heating methyl *iso*fenchylxanthate, its amide, or the liquid *iso*fenchylxanthamide which probably contains a mixture of esters, at 160—180°. The products obtained gave the following constants: (i) from the ester, b. p. 139—140°/760 mm.; d_4^{20} 0·8381; n^{20} 1·4494; $[\alpha]_D$ −68·76° in alcohol; (ii) from the solid amide, b. p. 140—141°/740 mm.; d_4^{20} 0·8397; n^{20} 1·4502; $[\alpha]_D$ −57·28° in alcohol; (iii) from the liquid amide, b. p. 140·5—141·5°/740 mm.; d_4^{20} 0·8398; n^{20} 1·4505; $[\alpha]_D$ −50·98°. Fenchylene has the lowest boiling point of all the hydrocarbons of formula $C_{10}H_{16}$; it differs also from *cyclo*fenchene and fenchene in its lower specific gravity and refractive index. The differences between the three preparations of fenchylene are probably due to the presence of varying amounts of a hydrocarbon of higher boiling point, specific gravity, and refractive index, but of lower specific rotatory power, probably *cyclo*fenchene. Fenchylene combines readily with bromine to give an oily product which cannot be solidified. With ethyl nitrite in acetic acid solution it yields a crystalline *nitrosyl chloride*, $C_{10}H_{16}NOCl$, m. p. 131°. Alkaline permanganate oxidises it to *cis*-fenchocamphoric acid. F. G. P.

Pinene. V. Preparation of α- and δ-Pinene. L. Ruzicka and S. Pontalti (*Helv. Chim. Acta*, 1924, 7, 489—495).—To complete the partial synthesis of *dl*-α-pinene, of which two stages have already been described (Ruzicka and Trebler, A., 1921, i, 36, 796), it was necessary to establish the genetic relationship between pinocamphone and pinocamphylamine. The latter was therefore prepared from pinocamphone by Wallach's method (A., 1901, i, 90) and methylated to pinocamphyltrimethylammonium iodide, m. p. 231°. The m. p. of this compound differs from that of previous preparations of Ruzicka and Trebler (m. p. 255°), and is probably a different mixture of *cis*- and *trans*-isomerides. When the pinocamphyltrimethylammonium hydroxide was distilled in a high vacuum it gave pinocamphyldimethylamine (which when treated with methyl iodide gave the parent substance with unchanged m. p., 231°) and a hydrocarbon. The latter when oxidised gave a mixture of pinonic acid, proving the presence of α-pinene, and an acid, m. p. 186—187°, identical with that obtained by Wallach (A., 1906, i, 683) by oxidation of *dl*-pinocamphone. This acid, for which the name pinocamphoric acid is proposed, must have the formula,  $CH\left\langle\begin{array}{l}CH{\cdot}CHMe{\cdot}CO_2H\\ \quad >CMe_2\\ CH{\cdot}CO_2H\end{array}\right.$, and proves the presence of δ-pinene (cf. Blumann and Zeitschel, A., 1921, i, 426). The dicarboxylic acid, m. p. 192°, obtained by Gildemeister and Köhler (A., 1910, i, 180) by oxidising a hydrocarbon obtained by the decomposition of *l*-pinocamphyl xanthate prepared from pinocamphone from hyssop oil, is shown to be identical with pinocamphoric acid. *l*-Pinocamphone was converted by the above reactions into a mixture of α- and δ-pinene, giving a mixture of pinonic and pinocamphoric acid (m. p. 192°) on oxidation. The dihydroverbenene of Blumann and Zeitschel (*loc. cit.*) is probably not δ-pinene, but contains an active form of α-pinene. E. H. R.

Terpenes and Ethereal Oils. CXXVIII. Condensation of Intracyclic Ketones with Two Mols. of Aromatic Aldehydes. O. WALLACH (*Annalen*, 1924, **437**, 187—189; cf. A., 1899, i, 532).—Dicyclic ketones having a methylene group adjacent to the carbonyl group and in which by rupture of the bridge linkings a second methylene group vicinal to the carbonyl can be formed, condense with aromatic aldehydes in the presence of hydrochloric acid, yielding chlorodibenzylidene compounds. Thus nopinone and benzaldehyde yield 3 : 5-*dibenzylidene-α-chloro*iso*propyl*cyclo*hexan-4-one*, yellow needles, m. p. 148—149°, the bridge ring being first ruptured by addition of hydrogen chloride, followed by condensation with two molecules of aldehyde :



In the presence of alkali, nopinone and benzaldehyde yield the monobenzylidene derivative, m. p. 106° (cf. A., 1901, i, 89), which with benzaldehyde and hydrochloric acid in alcoholic solution yields the dibenzylidene derivative. Similarly, verbanone yields a *chlorodibenzylidene* derivative, $C_{24}H_{25}OCl$, m. p. 143°, and sabina ketone a *chlorodibenzylidene* derivative, $C_{23}H_{25}OCl$, m. p. 157°, and with anisaldehyde a condensation *product*, m. p. 198°. R. B.

Terpenes and Ethereal Oils. CXXIX. Review of the Boiling Points of Stereoisomeric Modifications of Alicyclic Compounds. O. WALLACH (*Annalen*, 1924, **437**, 190—194; cf. A., 1893, i, 274; 1898, i, 485; 1913, i, 482; 1915, i, 423).—The boiling points of *l*- and *d*-menthone as given by various authors fluctuate between 204° and 210°. A careful redetermination under exactly comparable conditions gives the b. p. 210—210·25° for *l*-menthone and 210·5° for *dl*-menthone. Attempts to determine the boiling points of the different menthonoximes gave no satisfactory results, and it is doubtful whether stereoisomeric compounds can be distinguished from one another by their boiling points. The semi carbazone (m. p. 209°) from trimethyl*cyclo*pentanone (A., 1915, i, 499) was separated by crystallisation into two fractions, m. p. 178° and 214°, which on decomposition with oxalic acid yield *ketones*, b. p. 162—168°, and 167—171°, giving *oximes*, m. p. 78° and 110°, respectively. The original trimethyl*cyclo*pentanone (b. p. 164—167°, oxime, m. p. 105°) is evidently a mixture, but it was not possible to decide from these results whether the isomerism was purely physical, or chemical through the formation of the two theoretically possible isomerides, 1 : 1 : 2-trimethyl*cyclo*pentan-4-one and 1 : 1 : 4-trimethyl*cyclo*pentan-2-one. R. B.

Essential Oils from *Leptospermum Liversidgei*. A. R. PENFOLD (*J. Roy. Soc. New South Wales*, 1922, **56**, 82—87).—There appear to be two, and probably three, distinct forms of this shrub, yielding, respectively, 0·25—0·3% of oil with 35—50% of citral (no citronellal; cf. Baker and Smith, *ibid.*, 1905, **39**, 124), about 0·55% of oil containing 70—80% of citronellal (no citral), and about 0·6—0·8% of oil containing about 70—80% of citral (no citronellal ?).

W. T. K. B.

A New Stearopten occurring in some Essential Oils of the *Myrtaceæ*. A. R. PENFOLD and F. R. MORRISON (*J. Roy. Soc. New South Wales*, 1922, **56**, 87—89).—The essential oils of *Bæckea crenulata* and *Darwinia grandiflora* contain 5·5% and 2%, respectively, of a solid crystallising from alcohol in primrose-yellow needles or monoclinic prisms, m. p. 103—104°. Its solution in alcohol is optically inactive. The compound appears to have the formula $C_{13}H_{18}O_4$, and to contain two methoxy groups; it is considered to be a phenol ether. W. T. K. B.

Miscibility Test for Eucalyptus Oils. C. E. FAWSITT and C. H. FISCHER (*J. Roy. Soc. New South Wales*, 1922, **56**, 109—114).—The determination of the critical solution temperature by mixing the oil in definite proportions with a suitable liquid (*e.g.*, aqueous alcohol) giving two layers at the ordinary temperature, heating until only one layer is formed, and then allowing to cool until a cloudiness develops, affords a more sensitive test than the method in which the volume of aqueous alcohol required for complete solution of one volume of the oil is determined. [Cf. *B.*, 1924, 536.]

W. T. K. B.

Australian *Melaleucas* and their Essential Oils. VI. R. T. BAKER and H. G. SMITH (*J. Roy. Soc. New South Wales*, 1922, **56**, 115—124).—The oil from *Melaleuca ericifolia* (yield 0·84%) differs from oil of cajuput, by having a lower sp. gr. (d^{15} 0·8938), by the terpenes being strongly dextrorotatory, by containing *d*-terpineol in some quantity, by containing considerably less cineol, and by the principal oxygenated constituent being terpineol and not cineol. It has $[\alpha]_D$ +13·3°, n^{20} 1·4705, and saponification value 6·96. The oil obtained from young growths of *M. Deanei* (yield 0·7%) consists mainly of *d*-pinene, with only a small amount of oxygenated substances. The crude oil has d^{15} 0·8888, $[\alpha]_D$ +22·7°, n^{22} 1·4646, and saponification value 5·7. W. T. K. B.

Essential Oil of *Backhousia myrtifolia* [Grey or "Scrub" Myrtle]. I. A. R. Penfold (*J. Roy. Soc. New South Wales*, 1922, **56**, 125—129).—When the leaves and terminal branchlets of this tree are distilled with steam a brownish-yellow oil of pleasing odour and d^{15} 1·026—1·057 is obtained in an average yield of 0·42%, this being greatest in spring. The oil contains 75—80% of the rare phenol ether elemicin, together with pinene, a paraffin (m. p. 62—63°), a sesquiterpene, b. p. 120—138°/10 mm., an alcohol, b. p. 95—109°/10 mm., d^{15} 0·9018, rotation +7·6°, n^{20} 1·4770, and a phenol (0·24—0·5%). W. T. K. B.

Oak Moss Oil. H. Walbaum and A. Rosenthal (*Ber.*, 1924, **57**, [*B*], 770—773).—The odoriferous substance obtained by extraction or steam distillation of oak moss has been identified as orcinol monomethyl ether. The oil also contains ethyl β-orcinolcarboxylate (methyl 2 : 4-dihydroxy-3 : 6-dimethylbenzoate), m. p. 142°. By extracting the lichen with alcohol, ethyl everninate (6-hydroxy-4-methoxy-2-methylbenzoate), m. p. 76°, was isolated, but it is probable that the free acid occurs in the lichen and is esterified by the alcohol. Everninic acid may be the parent substance of the monomethyl orcinol. R. B.

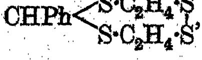
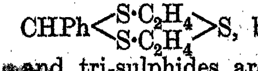
Refractive Index of Caoutchouc. D. F. Twiss (*Nature*, 1924, **113**, 822).—Caoutchouc has n_D^{15} 1·525. A. A. E.

The African Poison, Acocantherine. J. Moir (*J. S. Afr. Chem. Inst.*, 1924, **7**, 28—33).—Acocantherine, prepared from *Acokanthera venenata*, dissolves in concentrated sulphuric acid yielding an orange-yellow solution showing an absorption band at λ 476; after some time the colour darkens, a green fluorescence develops, and a band appears at λ 495. When hydrolysed with 2% sulphuric acid it yields rhamnose and acocanthic acid lactone; the latter gives a fluorescent orange-coloured solution in concentrated sulphuric acid with a band at λ 470, and a yellow solution in sodium hydroxide solution with a band at λ 440. Acocantherine therefore resembles ouabaine, and there is but little difference between the properties of acocanthic acid and those of the synthetic substance *benzoumbelliferone* (2 : *4-dihydroxydiphenyl-2′-carboxylic acid lactone*). W. P. S.

Insecticides. X. Synthesis of Pyrethrines. H. Staudinger and L. Ruzicka (*Helv. Chim. Acta*, 1924, **7**, 448—458).—Both active constituents of insect powder (this vol., i, 700) have been synthesised from their acid and alcoholic components, but the synthesis is incomplete, as synthetic chrysanthemumic acid has not yet been resolved and pyrethrolone has not been completely synthesised (cf. i, 522). Pyrethrine I, from chrysanthemumcarboxylic chloride and pyrethrolone in presence of pyridine, is a colourless, viscous oil, b. p. 145—150°/0·125 mm., $[\alpha]_D^{18}$ $-16·2°$; the semicarbazone is crystalline, but melts indefinitely between 80° and 90°. Pyrethrine II, obtained similarly from the chloride of methyl hydrogen chrysanthemumdicarboxylate, is a colourless, odourless, viscous oil, b. p. 195°/0·167 mm.; its semicarbazone is amorphous. A large number of esters of pyrethrolone with organic acids and of chrysanthemumcarboxylic acids with alcohols of many types were prepared, but none of these had insecticidal properties at all comparable with those of the pyrethrines. E. H. R.

Furoyl Peroxide. H. Gelissen and J. D. van Roon (*Rec. trav. chim.*, 1924, **43**, 359—366).—*Furoyl peroxide*, $(C_4H_3O·CO)_2O_2$, white crystals, m. p. 86°, which turn yellow in the air, is prepared by the action of cold alkaline hydrogen peroxide on pyromucyl chloride. It is less stable than benzoyl peroxide, is hydrolysed by water, and liberates iodine from potassium iodide solution. It is also more sensitive to shock than benzoyl peroxide, and explodes without smoke. Diphenyl can be obtained by warming benzoyl peroxide in benzene solution, but difuryl is not analogously formed from furoyl peroxide. E. H. R.

Trimethylene Trisulphides. O. Hinsberg (*Ber.*, 1924, **57**, [*B*], 836—838; cf. A., 1914, i, 185, 797; 1923, i, 1056).—The sulphoxide obtained by the action of hydrogen peroxide on trimethylene trisulphide $(CH_2S)_3$, is smoothly oxidised by permanganate in faintly acid solution to yield trimethylene trisulphone, $(CH_2SO_2)_3$ (cf. Fromm and Schultis, A., 1923, i, 580). The sulphoxide must therefore be the trimeric form, $(CH_2SO)_3$. Since hydriodic acid converts it into the trisulphide of m. p. 247°, and since it is re-formed from the latter by oxidation with hydrogen peroxide, this trisulphide must be trimeric, and stereoisomeric with that of m. p. 216°. Possibly the crude trisulphide forms a third stereoisomeride which changes into the 216° form on crystallisation. F. A. M.

Synthesis of Cyclic Polysulphides. I. Sir P. C. Rây (*J. Chem. Soc.*, 1924, **125**, 1141—1144).—When dithioethylene glycol (2 mols.) and benzylidene chloride (1 mol.) are boiled together gently during 30 hours, the chief products are *benzylidenediethylene tetrasulphide*,  $CHPh<\begin{matrix}S·C_2H_4·S\\ |\\ S·C_2H_4·S\end{matrix}$, and *trisulphide*,  $CHPh<\begin{matrix}S·C_2H_4\\ S·C_2H_4\end{matrix}>S$, both of which are oily liquids; diethylene di- and tri-sulphides are also formed as by-products. According to the duration of heating, benzylidenediethylene trisulphide reacts with boiling methyl iodide to form *methiodides* approximating in composition to $C_4H_8S_2$,2MeI and C_4H_8S,3MeI; with ethyl iodide it forms an *ethiodide*, $2C_{11}H_{14}S_2$,EtI, together with diethylene di- and tri-sulphides.

With mercuric chloride and platinic chloride, benzylidenediethylene tri- and tetra-sulphides form additive compounds; in the substances formed from platinic chloride, the valency of platinum may vary (cf. T., 1923, **123**, 133).

Oxidation of benzylidenediethylene trisulphide with nitric acid yields benzoic acid, ethanedisulphonic acid, and sulphuric acid.
C. J. S.

Strychnine and Brucine. R. CIUSA and G. SCAGLIARINI (*Gazzetta*, 1924, **54**, 202—203).—The authors reply to Oliveri-Mandalà and Comella (A., 1923, i, 1223) on certain points concerning the structure of *iso*strychnine. T. H. P.

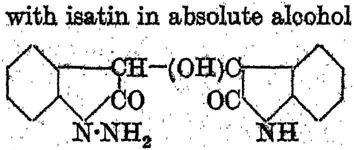
[Partial] Synthesis of 2-*n*-Butylpyrrolidine. E. E. BLAISE and A. CORNILLOT (*Compt. rend.*, 1924, **178**, 1186—1188; cf. Blaise and Houillon, A., 1906, i, 692, also following abstract).—Magnesium *n*-butyl iodide converts ethyl cyanoacetate into *ethyl* n-*valerylacetate*, b. p. 112°/18 mm., converted by semicarbazide and phenylhydrazine into the *carbamylpyrazolone*, m. p. 165°, and *butylphenylpyrazolone*, m. p. 79°, respectively. The potassium derivative of the valeryl ester reacts with β-iodoethylphthalimide to give a compound which when hydrolysed with hydrobromic acid affords 2-n-*butylpyrroline*, b. p. 68·5°/19 mm. [*chloroplatinate*, m. p. 182—183° (decomp.)]. The hydrochloride reacts with potassium cyanate, yielding the *carbamide*, $C_9H_{16}ON_2,H_2O$, m. p. 104—105°. Hydrogenation of the base has not yet been effected. H. J. E.

Synthesis of 2-*n*-Butylpyrrolidine. E. E. BLAISE and A. CORNILLOT (*Compt. rend.*, 1924, **178**, 1617—1619).—2 : 5-Dimethylpyrroline, obtained by reducing the product of the interaction of ammonia and acetonylacetone, forms a chloroaurate, m. p. 77° [Knorr and Rabe (A., 1902, i, 54) gave 68—69°], and a phenylcarbamide, m. p. 130°. When reduced in an atmosphere of hydrogen and in presence of platinum chloride previously reduced by means of gum arabic, it yields 2 : 5-dimethylpyrrolidine as a colourless liquid, b. p. 106·5°; the chloroaurate has m. p. 85° [Fenner and Tafel (A., 1900, i, 111) gave 96—100°] and the phenylcarbamide, m. p. 142°. 2-*n*-Butylpyrrolidine, similarly prepared from 2-*n*-butylpyrroline, agrees exactly with the compound previously obtained by Blaise and Houillon (A., 1906, i, 692), so that Hess' compound (A., 1920, i, 85) must have another constitution. It is suggested that the use of hydriodic acid as a reducing agent should be avoided in all synthetic processes used for the determination of constitution. T. H. P.

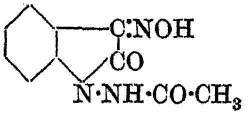
Nitropyrrole and Pyrrole-aldehydes. A. ANGELI (*Ber.*, 1924, **57**, [*B*], 834—836).—A criticism of recent work by Fischer, Zerweck, and Smeykal (A., 1922, i, 758; this vol., i, 201); their statement that alkylated pyrroles can be nitrated smoothly is not strictly accurate, as they worked with carboxylic esters of pyrrole-ketones and -aldehydes, dicarboxylic esters, etc. Angeli had already shown that pyrrole, but not methyl pyrryl ketone, is rapidly oxidised by permanganate. Fischer and Zerweck overlooked Angeli's synthesis of pyrrole-aldehydes using formic ester and sodium alkoxide, which favours a hydroxymethylene structure for these substances (cf. A., 1915, i, 454; and Fischer, A., 1913, i, 1225). Pyrrole-aldehyde and its di-ortho substituted derivatives do not respond to Baudisch's reagent (A., 1921, ii, 337), whereas 1-methylpyrrole-aldehyde does. F. A. M.

1-Amino-oxindole. P. W. NEBER and H. KEPPLER (*Ber.*, 1924, **57**, [*B*], 778—787).—1-Amino-oxindole (A., 1922, i, 546) on treatment with 1 or 2 mols. of benzaldehyde yielded 1-*amino-3-benzylideneoxindole* (pale yellow crystals, m. p. 116°) or 1-*benzylideneamino-3-benzylideneoxindole* (yellow needles, m. p. 161°), respectively. The monobenzylidene compound with amyl nitrite and hydrochloric acid gave 3-benzylideneoxindole, m. p. 172° (cf. Wahl and Bagard, A., 1909, i, 735). With the three nitrobenzaldehydes the products were the 1-nitrobenzylideneamino-oxindoles, which were conveniently prepared from the corresponding nitrobenzylidenephenylhydrazine-*o*-acetic acids. N′[*o-Nitrobenzylidene*]-*phenylhydrazine*-o-*acetic acid* forms orange needles, m. p. 158°; the *meta* compound forms orange leaflets, m. p. 166°, the *para* compound scarlet needles, m. p. 175°; boiling glacial acetic acid converts the acids into the corresponding 1-*nitrobenzylideneamino-oxindoles*, which form yellow needles, *ortho*, m. p. 168—170°; *meta*, m. p. 160°; *para*, m. p. 220—227°. These are stable to mineral acids and insoluble in alkalis. The *o*-nitrobenzylidene compound on treatment with amyl nitrite and hydrochloric acid affords β-isatoxime.

1-Amino-oxindole condensed with isatin in hot acetic acid to form N-*amino*iso*indigotin*, yellow needles, m. p. 205—207°; this gave the indophenin reaction. 1-Acetamido-oxindole also condensed with isatin to form N-*acetamido*iso*indigotin* (a bright red, microcrystalline powder, m. p. 303—306° [indef.]), which dissolved easily in dilute alkali, from which it was reprecipitated by acids. A solution of *N*-amino*iso*indigotin in aqueous potassium hydroxide on acidification gave a *substance*, $C_{16}H_{13}O_3N_3$, golden-yellow leaflets, m. p. 234—236°, which was insoluble in sodium carbonate but soluble in warm dilute alkali. On condensing 1-amino-oxindole with isatin in absolute alcohol in presence of piperidine a *substance* (annexed formula), was obtained as ivory-coloured leaflets, m. p. (decomp.) 208° upwards. On heating with alcoholic potassium hydroxide and acidifying, the yellow *isomeride*, $C_{16}H_{13}O_3N_3$, m. p. 234—236°, was obtained. N-*Aminoindirubin* was obtained by condensing 1-amino-oxindole and isatin-α-anil in alcoholic solution and formed almost black needles, m. p. (indef.) 253—256° (with previous sublimation). N-*Acetamidoindirubin* was obtained similarly from 1-acetamido-oxindole and isatin-α-anil as reddish-violet needles, m. p. about 299—302° (with previous sublimation). 1-*Acetamido-oxindole* forms colourless needles (+1H₂O), m. p. 186—187°. 1-*Benzoylamido-oxindole* forms faintly coloured leaflets, m. p. 189°. Both the acetyl and benzoyl com-

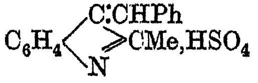


pounds are soluble in dilute alkalis. Treatment of 1-acetamido-oxindole in acetic acid with amyl nitrite and hydrochloric acid gave bright green needles of N-*acetamido-β-isatoxime* (annexed formula), m. p. 245—246° (decomp.); this, when boiled with sulphuric acid (1 : 3), afforded indazole-3-carboxylic acid. Condensation of 1-acetamido-oxindole with *p*-nitrosodimethylaniline gave N-*acetamido-isatin-β*-p-*dimethylamino-anil* as a dark brown powder, m. p. 214° (with previous sublimation) (red *sodium* salt, soluble), which with dilute mineral acids gave indazolecarboxylic acid. 1-Acetamido-oxindole was converted by dimethyl sulphate into 1-*acetyl-methylamino-oxindole*, colourless leaflets, m. p. 146°; treatment with amyl nitrite and hydrochloric acid gave N-*acetylmethyl-amino-β-isatoxime*, greenish-yellow needles, m. p. 192—194° (*methyl ether*, yellowish-brown leaflets, m. p. 205—207°; also obtained directly by methylation of *N*-acetamido-β-isatoxime). On boiling the oxime with dilute sulphuric acid, 2-*methylindazole-3-carboxylic acid* was obtained as colourless leaflets, m. p. 215° (decomp.). Complete methylation of 1-amino-oxindole afforded 1-*dimethylamino-oxindole* as colourless leaflets, m. p. 81°; this condensed with nitrosobenzene in presence of piperidine to give N-*dimethylaminoisatin-3-anil*, orange needles, m. p. 125°, which when hydrolysed gave N-*dimethylaminoisatin*, dark red needles, m. p. 239°. 1-Dimethylamino-oxindole on treatment with amyl nitrite in hydrochloric–acetic acid solution afforded N-*di-methylamino-β-isatoxime*, yellow needles, m. p. 166—167°.

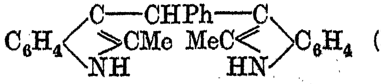


F. A. M.

The Humin formed by Acid Hydrolysis of Proteins. VIII. Condensation of Indole Derivatives with Aldehydes. G. O. BURR and R. A. GORTNER (*J. Amer. Chem. Soc.*, 1924, **46**, 1224—1246; cf. Freund and Lebach, A., 1905, i, 663).—2-Methylindole condenses with benzaldehyde in presence of concentrated sulphuric acid to form *phenyl-2-methylindolidenemethane hydrogen sulphate* (I), orange needles, darkening above 100°, m. p. 172—173° with re-solidification at 175°. The free base was amorphous. On boiling with water, the sulphate is converted into phenyldi-2-methylindylmethane (II) (Fischer's "benzylidene dimethyl ketole") and benzaldehyde, the reaction being reversed in presence of concentrated sulphuric acid.

(I.)


$$C_6H_4\left<\begin{matrix}C{:}CHPh\\N\end{matrix}\right>CMe,HSO_4$$


(II.)

$$C_6H_4\left<\begin{matrix}C\\NH\end{matrix}\right>CMe\overset{\text{—CHPh—}}{\ }MeC\left<\begin{matrix}C\\HN\end{matrix}\right>C_6H_4$$

p-*Dimethylaminophenyl-2-methylindolidenemethane hydrochloride*, similarly obtained using hydrogen chloride as condensing agent, forms a hard, golden mass, m. p. 150—160°, purple-red in solution. The *base* has m. p. about 100°, dependent on the rate of heating. Its alcoholic solution is colourless at p_H 7·58, brilliant red at p_H 6·48. It yields a humin-like material on treatment with alcoholic hydrogen chloride, and both substances form ferrocyanides of the composition $(Base)_4,H_4Fe(CN)_6,2H_2O$. The violet humin-like base similarly obtained from *o*-hydroxyphenyl-2-methylindolidenemethane has m. p. 305°. *Anisyl-2-methylindolidenemethane hydrochloride*, golden, irregular plates, m. p. 181° (darkening at 155°); *cinnamyl-2-methylindolidenemethane hydrochloride*, golden needles, blackening at 160°, sintering at 180°, m. p. 195—205°; o-*tolyl-2-methylindolidenemethane hydrochloride*, yellow prisms, m. p. 178° (darkening at 165°); p-*hydroxyphenyl-2-methylindolidenemethane hydrochloride*, orange-red plates and wedges, m. p. 189°; m-*nitrophenyl-2-methylindolidenemethane*, a brown powder, exploding at a high temperature; and 2 : 4 : 6-*trinitrophenyl-2-methylindolidenemethane*, minute, orange needles, m. p. 152°, are described. 2-Phenylindole condenses with benzaldehyde (excess) in presence of sulphuric acid, to form Fischer's "benzylidene-Pr_2-phenylindol." Using excess of sulphuric acid, *phenyl-2-phenylindolidenemethane* is formed as an orange powder, m. p. 182—184°, hydrolysed by boiling water to *benzylidenedi-2-phenylindole*. p-*Hydroxyphenyl-2-phenylindolidenemethane hydrochloride*, red prisms, m. p. indef.; *cinnamyl-2-phenylindolidenemethane*, a brown powder, m. p. 146—148°; o-*hydroxyphenyl-2-phenylindolidenemethane hydrochloride*, minute needles, sintering at 165°, but having no m. p.; o-*chlorophenyl-2-phenylindolidenemethane hydrochloride*, an orange powder, m. p. 212—214°; *anisyl-2-phenylindolidenemethane*, a red powder, m. p. indef.; p-*dimethylaminophenyl-2-phenylindolidenemethane*, a purple powder, m. p. 155°; o-*tolyl-2-phenylindolidenemethane*, a brownish-yellow powder; m-*nitrophenyl-2-phenylindolidenemethane*, a yellow powder; and 2 : 4 : 6-*trinitrophenyl-2-phenylindolidenemethane*, an unstable, orange powder, are described. 2 : 3-Diphenylindole gave no condensation products analogous with the above, benzaldehyde etc. giving a grey, powdery *substance*, m. p. 123°. 2-Phenyl-3-methylindole yielded, similarly, a grey *substance*, m. p. 221—223°. Tryptophan condenses with salicylaldehyde with formation of a grey, powdery *substance*, $C_{12}H_{24}O_5N_2Cl$, excess of the aldehyde giving a humin. Humin-like products, derived from the condensation of 1 mol. of the indole with 2 mols. of aldehyde, were obtained by boiling the indoles, or the primary condensation products analogous to (I) and (II) above, with excess of the appropriate aldehyde in 20% hydrochloric acid. Yields were generally quantitative except with trinitrobenzaldehyde; humins were not obtainable from 2 : 3-diphenylindole. The solubilities of the humin hydrochlorides in acids, alkalis, and organic solvents, the solubility of the bases in ether, and their fusibility are tabulated. The artificial humins are precipitated from chloroacetic acid solution by water, but fibrin humins require the addition of hydrochloric acid to bring about coagulation. Humins of constant composition cannot be obtained from proteins. The humin from *o*-tolualdehyde and 2-methylindole was the most readily purified, whilst 2-phenylindole and benzaldehyde gave the only oxygen-free humin. The mol. weights of two fibrin humins, determined cryoscopically in chloroacetic acid, were found to be 439 and 760—780, respectively. Mol.-weight determinations of the indole humins in aniline were unsuccessful. In phenol, the values obtained indicated that humin formation from 1 mol. of indole and 2 mols. of aldehyde is accompanied by polymerisation of the simple end-product. In benzene, further association was found in the one case examined. The mol. weights of hydrolytic humins and those derived from aromatic aldehydes were of the same order, whilst those derived from formaldehyde and indoles were much higher. 2-Methylindole remains unchanged on boiling with 20% hydrochloric acid. Phenyl-2-methylindolidenemethane hydrogen sulphate loses 1 mol. of water at 140—150°, with formation of a sulphonic acid. It yields amorphous, reddish-violet products on boiling with acids or on exposing its solutions to the light of a tungsten lamp. Some of these products condense more readily with benzaldehyde than does the original substance, indicating that humin formation from the indolidenemethane intermediates is preceded by molecular rearrangement. The humins obtained from 2-methylindole and benzaldehyde, 2 : 4 : 6-trinitrobenzaldehyde, and *o*-tolualdehyde, respectively, were stable to alkaline permanganate or alkali fusion, but were completely oxidised (to benzoic acid) by boiling chromic-acetic acid. The *o*-tolualdehyde humin formed a black, amorphous *dibromide*, $C_{25}H_{21}NBr_2$, the humin being regenerated by the action of sodium in alcohol. An unstable hydrochloride, but no picrate, was obtained. F. G. W.

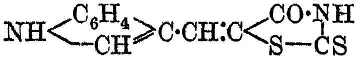
Isatin. Condensation of Isatin with Phenylhydroxylamine. H. Rupe and E. Stöcklin (*Helv. Chim. Acta*, 1924, 7, 557—566).—Isatin reacts readily with phenylhydroxylamine to form *isatinphenylhydroxylamine*, $C_6H_4{<}{}^{CO}_{N}{>}C{\cdot}NPh{\cdot}OH$, large, red needles, m. p. 216° (decomp.), which is decomposed by alkalis into isatinic acid and phenylhydroxylamine. The same compound is obtained from isatin chloride and phenylhydroxylamine. With methyl sulphate in presence of alkali it gives O-*methylisatin*-β-*phenylhydroxylamine*, long, orange prisms, m. p. 152° (decomp.). On one occasion an *isomeride*, probably the *N*-methyl derivative, brown crystals, m. p. 181° (decomp.), was obtained, which, unlike the *O*-ether, is readily hydrolysed by alkali. The O-*acetyl* derivative of isatinphenylhydroxylamine, long needles, m. p. 179° (decomp.), and the O-*benzoyl* derivative, orange needles, m. p. 196°, are stable in presence of alkali. By the action of thionyl chloride on isatinphenylhydroxylamine, *isatin*-N-*chloroanilide*, $C_8H_4ON{\cdot}NPh{\cdot}Cl$, is obtained, small, brownish-red tablets, m. p. 182°. Isatinphenylhydroxylamine reacts with phenylhydrazine and semicarbazide to form isatinphenylhydrazone and isatinsemicarbazone. 7-*Methylisatin*-β-*phenylhydroxylamine* forms dark red crystals, m. p. 222—225° (decomp.).

By condensing 5-nitroisatin with phenylhydroxylamine, or by nitrating isatinphenylhydroxylamine with nitric acid (*d* 1·35), *5-nitroisatinphenylhydroxylamine* is obtained, glistening bronze leaflets, m. p. 227° (decomp.). Its O-*methyl* ether forms orange, [illegible] 213°, and its *benzoyl* derivative, orange needles,

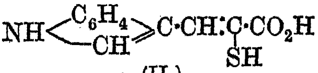
m. p. 203°. The nitro compound is readily soluble in alkalis, even in ammonia, with a deep red colour, and probably has the pseudo-acid structure, $\mathrm{NO_2H{\cdot}C_6H_3}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{N}}>\mathrm{C{:}NPh{:}O}$.

A new nitro derivative of isatin, 6-*nitroisatin*, obtained by nitrating isatin in concentrated sulphuric acid, forms reddish-yellow needles, m. p. 244°. 6-*Nitroisatin*-β-*phenylhydroxylamine* forms long needles, m. p. 224—227°, much redder than the 5-nitro derivative. E. H. R.

Use of Rhodanine in Organic Syntheses. IV. Indole- and Furyl-pyruvic Acids. C. GRÄNACHER, M. GERÖ, and V. SCHELLING (*Helv. Chim. Acta*, 1924, 7, 575—578; cf. A., 1923, i, 706, 713).—3-Indolealdehyde condenses with rhodanine in acetic acid or acetic anhydride to form 3-*indolylidenerhodanine* (I), glistening brown leaflets, decomposing above 200°. This substance is converted by hot potassium hydroxide solution into α-*thiol*-β-3-*indoleacrylic acid* (II), an orange powder, decomp. 190°. When the ammonium salt of this acid is warmed in solution with lead powder, it is converted into β-3-indolepyruvic acid, $C_8H_6N{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$.


$\mathrm{NH}<\genfrac{}{}{0pt}{}{\mathrm{C_6H_4}}{\mathrm{CH}}>\mathrm{C{\cdot}CH{:}C}<\genfrac{}{}{0pt}{}{\mathrm{CO{\cdot}NH}}{\mathrm{S{-}CS}}$

(I.)


$\mathrm{NH}<\genfrac{}{}{0pt}{}{\mathrm{C_6H_4}}{\mathrm{CH}}>\mathrm{C{\cdot}CH{:}}\underset{\mathrm{SH}}{\mathrm{C}}\mathrm{{\cdot}CO_2H}$

(II.)

β-2-*Furylpyruvic acid* has been obtained by hydrolysing α-oximino-β-2-furylpyruvic acid (A., 1922, i, 850) with sulphurous acid. It forms unstable, pale yellow needles, m. p. 131°. E. H. R.

Use of Rhodanine in Organic Syntheses. V. Indole-2-carboxylic acid. C. GRÄNACHER, A. MAHAL, and M. GERÖ (*Helv. Chim. Acta*, 1924, 7, 579—586).—A new synthesis of indole-2-carboxylic acid is described. *o*-Nitrobenzylidenerhodanine (Bondzyński, A., 1887, 1108) is reduced in aqueous solution with ferrous hydroxide, and the solution of *o*-aminobenzylidenerhodanine, after making strongly alkaline with sodium hydroxide, is filtered and boiled, whereby α-thiol-*o*-aminocinnamic acid is formed. Ammonium chloride is added in small portions, whereupon a vigorous reaction ensues, and the resulting indole-2-carboxylic acid is precipitated by acidification. Ethyl indole-2-carboxylate (m. p. 124—125°) condenses with benzaldehyde to form *ethyl phenyl*-3 : 3′-*di-indylmethane*-2 : 2′-*dicarboxylate*, $CHPh(C_8H_5N{\cdot}CO_2Et)_2$, white needles, m. p. 239°; the corresponding *acid* crystallises in needles containing 1 mol. of alcohol, m. p. 243—244° (decomp.); *potassium* salt, $C_{25}H_{16}O_4N_2K_2,H_2O$. Similarly, *p*-anisaldehyde condenses to give *ethyl* p-*methoxyphenyl*-3 : 3′-*di-indylmethane*-2 : 2′-*dicarboxylate*, white crystals, m. p. 222° (decomp.); the corresponding *acid* has m. p. 267° (decomp.), and turns red on exposure to air. Formaldehyde condenses with ethyl indole-2-carboxylate to give, in poor yield, *ethyl* 3 : 3′-*di-indylmethane*-2 : 2′-*dicarboxylate*, a yellow, crystalline powder, m. p. 260° (decomp.); the *acid* forms pale yellow needles containing 1 mol of alcohol, m. p. 265°. E. H. R.

Formation of 3-Halogencarbazoles from Carbazole-3-diazonium Halides. S. H. Tucker (*J. Chem. Soc.*, 1924, **125**, 1144—1148).—Carbazole-3-diazonium chloride has been obtained (cf. T., 1922, **122**, 2711) anhydrous and as di- and trihydrates. When treated, in acetone solution, with copper–bronze it yields a yellow product which, when acetylated, yields 3-chloro-*N*-acetylcarbazole, and this on hydrolysis gives 3-chlorocarbazole. *Carbazole-3-diazonium bromide*, $C_{12}H_8N_3Br,2H_2O$, yellow crystals, m. p. 110° (decomp.), was prepared from 3-aminocarbazole, and also from carbazole-3-diazonium chloride and potassium bromide; by treatment, in methyl ethyl ketone, with copper-bronze and acetylating and hydrolysing the resulting product there is formed 3-bromocarbazole. 3-Acetoxy-*N*-acetylcarbazole is obtained when carbazole-3-diazonium bromide is boiled with acetic anhydride and a little concentrated sulphuric acid.

Carbazole-3-diazonium iodide, $C_{12}H_8N_3I,H_2O$, is precipitated as a canary-yellow, crystalline substance on mixing aqueous solutions of carbazole-3-diazonium chloride and potassium iodide. It decomposes spontaneously in organic solvents to form 3-*iodocarbazole*, colourless, nacreous plates, m. p. 192—194° (N-*acetyl* derivative, needles, m. p. 145—147°). C. J. S.

Condensation of Acetaldehyde with Ammonia in Presence of Alumina. A. E. Tschitschibabin, P. A. Moschkin, and L. S. Tjaschelowa (*J. pr. Chem.*, 1924, [ii], **107**, 132—137).—The product obtained by passing acetaldehyde and ammonia over alumina at 300° resembled closely that from acetylene and ammonia (this vol., i, 313). The crude condensate contained neutral compounds (20—25%), secondary bases, and tertiary bases (42½% of the raw condensate or about 60% of the theoretical yield). Further examination was confined to the last mixture; it was fractionally distilled and then separated into its components by fractional precipitation of their picrates (cf. *loc. cit.*). α-Picoline, γ-picoline, and 2-methyl-5-ethylpyridine ("aldehyde-collidine") were present in nearly equal amounts, together with smaller quantities of β-collidine and the two other bases already described (*loc. cit.*). There were no indications that pyridine was formed. W. A. S.

Products formed when Paraldehyde and Aldehyde-ammonia are heated together. A. E. Tschitschibabin and M. P. Oparina (*J. pr. Chem.*, 1924, [ii], **107**, 138—144).—For comparison with the results obtained in other experiments (cf. foregoing abstracts) this condensation (Dürkopf and Schlaugk, A., 1888, 1314, etc.) has been reinvestigated. A mixture of paraldehyde (3 mols.) and aldehyde-ammonia (1 mol.), heated in a sealed tube for 4 hours at 220°, gives an oily product, one-third of which is insoluble in acid. The remainder, separated into its components by fractional distillation and precipitation with picric acid, consists (above 80%) of 2-methyl-5-ethylpyridine; about 11% is α-picoline, whilst γ-picoline and β-collidine are also present in small amount. There is also a little of the collidine (the picrate is now stated to [illegible]59° and the chloroplatinate m. p. 190°) found in the product of interaction of acetaldehyde and ammonia in presence of alumina. The trimethylpyridine of Knudsen and others (A., 1895, i, 562) and lutidine were not detected. W. A. S.

Condensation of Propionaldehyde with Ammonia. A. E. TSCHITSCHIBABIN and M. P. OPARINA (*J. pr. Chem.*, 1924, [ii], **107**, 145—154).—By passing propionaldehyde and ammonia over alumina at 310—320°, a product was obtained which consisted of neutral substances (about 50%), secondary bases (about 15%), and tertiary bases, the yield of which therefore was about 40% of the theoretical, in agreement with that obtained by other methods (cf. Dürkopf and others, A., 1890, 1002, etc.). The mixture of tertiary bases contained some tarry material of high b. p., but otherwise consisted almost entirely of the following three compounds: 3 : 5-dimethyl-2-ethylpyridine (picrate, yellow leaflets, m. p. 156—157°, cf. Dürkopf, *loc. cit.*), about 60%; 3 : 5-*dimethyl*-4-*ethylpyridine* (b. p. 219—220°/748 mm., $d_4^{26\cdot7}$ 0·9516, $n_D^{26\cdot7}$ 1·5064; *picrate*, prisms, m. p. 155—156°), about 23%; this substance was isolated by Dürkopf (*loc. cit.*), who supposed it to be a tetramethylpyridine; the authors have now oxidised it to 4-*ethylpyridine*-3 : 5-*dicarboxylic acid*, m. p. 261° (decomp.), and converted the latter into 4-ethylpyridine (cf. Tschitschibabin, A., 1906, i, 451). The remaining 17—18% of the mixture is 3 : 5-dimethylpyridine. W. A. S.

Synthesis of Pyridine from Aldehydes and Ammonia. A. E. TSCHITSCHIBABIN and M. P. OPARINA (*J. pr. Chem.*, 1924, [ii], **107**, 154—158).—A more detailed account of work already noted (this vol., i, 312). W. A. S.

2-Amino-4-methylpyridine and certain Derivatives. O. SEIDE (*Ber.*, 1924, **57**, [*B*], 791—794; cf. Tschitschibabin and Zeide, A., 1915, i, 590; Zeide, A., 1923, i, 600).—2-*Amino*-4-*methylpyridine*, lustrous leaflets, m. p. 98°, is prepared by the action of sodamide on 4-methylpyridine dissolved in boiling xylene; the *hydrochloride*, m. p. 176—177°, *nitrate*, m. p. 139°, *picrate*, m. p. 227° (decomp.), and *chloroplatinate*, m. p. 208°, are described. 2-*Acetylamino*-4-*methylpyridine*, colourless prisms, m. p. 102—103°, yields a *picrate*, yellow needles. Benzoylation of 2-amino-4-methylpyridine gives a mixture of the *dibenzoyl* derivative, colourless needles, m. p. 182—183°, and *monobenzoyl* compound, colourless prisms, m. p. 114°. Diazotisation of 2-amino-4-methylpyridine in very concentrated hydrochloric acid solution yields mainly 2-*chloro*-4-*methylpyridine*, a colourless liquid, b. p. 194—195°, d_4^{20} 1·1459, n_D^{8} 1·5293 [*chloroplatinate*, orange-coloured prisms ($+H_2O$) which blacken at 219° but do not melt below 290°]; 2-*hydroxy*-4-*methylpyridine*, rhombs, m. p. 130° (*monohydrate*, m. p. 65°), is produced in minor amount, but is more conveniently prepared by diazotisation of the amine dissolved in dilute hydrochloric acid. 4-Amino-2-methylpyridine dissolved in concentrated sulphuric acid is converted by nitric acid (*d* 1·4) at 0° into 2-*nitroamino*-4-*methylpyridine*, pale yellow prisms, m. p. 182° (decomp.), which is transformed by prolonged contact with sulphuric acid at the atmospheric temperature into a mixture of (?) 3-*nitro-2-amino-4-methylpyridine*, yellow needles, m. p. 136°, and (?) 5-*nitro-2-amino-4-methylpyridine*, yellow prisms, m. p. 220°. H. W.

Constitution of Roth's 2-Stilbazolealkine and Synthesis of 2-Stilbazole*iso*alkine. C. Räth (*Ber.*, 1924, **57**, [*B*], 840—842).—Pyridine-2-aldehyde (cf. Lénart, A., 1914, i, 574) is converted by magnesium benzyl bromide into 2-*α-hydroxy-β-phenylethylpyridine*, colourless cubes, m. p. 104° (the *hydrochloride*, leaflets, m. p. 152°, and the non-crystalline *picrate* are described). It is not identical with the compound described by Roth (A., 1901, i, 165), which must therefore be 2-β-hydroxy-β-phenylethylpyridine. H. W.

Dihydroquinoline Bases. G. Heller (*Ber.*, 1924, **57**, [*B*], 764; cf. Räth, this vol., i, 555).—The compound considered by Doebner (A., 1898, i, 384) to be 2-methyldihydroquinoline should be deleted from the literature (cf. Heller and Sourlis, A., 1908, i, 914; Heller, A., 1911, i, 747). H. W.

Quinoline Dyestuffs. E. Rosenhauer [with A. Schmidt and W. Schleifenbaum] (*J. pr. Chem.*, 1924, [ii], **107**, 232—240).—2-Methylene-1-methyl-1 : 2-dihydroquinoline ("quinaldine*iso*-base") combines with bromine to form a perbromide-like compound, $C_{11}H_{11}NBr_3$ (yellow crystals, decomp. 152°), which decomposes when dissolved in acetone, giving bromoacetone and 2-*bromomethylquinoline methobromide*, pale yellow prisms, decomp. 205°. Either substance interacts with phenylhydrazine, giving 2-*benzeneazomethylene-1-methyldihydroquinoline hydrobromide*, violet needles, decomp. 250°; the corresponding *base* forms bronzy, dark red needles, m. p. 140—141°. Similar compounds were obtained with *p*-bromophenylhydrazine (*base*: red needles, m. p. [indef.] 162°; *hydrobromide*: needles, decomp. 259°) and *p*-nitrophenylhydrazine (*base*: bluish-green needles, decomp. 186°; *hydrobromide*: red needles, decomp. 248°). α-Bromomethylquinoline methobromide and *p*-aminodimethylaniline interact to give the *methobromide* (green prisms, decomp. 198°) corresponding with α-*p*-dimethylaminophenyliminomethylenequinoline ethiodide (Kaufmann and Valette, A., 1912, i, 655). The extension of these experiments to lepidine and α-picoline is announced. W. A. S.

1 : 1′-Dialkyltetrahydrodipyridyls. O. Mumm, O. Roder, and H. Ludwig (*Ber.*, 1924, **57**, [*B*], 865—880).—In continuation of previous work (Mumm and Beth, A., 1921, i, 686), the preparation is described of a 4 : 4′-disubstituted dipyridyl; it is bimolecular in freshly-prepared solution in freezing benzene, but gradually dissociates when preserved. It is intensely active chemically. Since, however, solutions which contain the unimolecular form are not intensely coloured, this activity is not ascribed to fission into [illegible] the powerful "divided" partial valencies of the [illegible] carbon atoms.

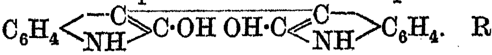
Ethyl 1 : 2 : 4 : 6 : 1′ : 2′ : 4′ : 6′-*octamethyltetrahydro*-4 : 4′-*dipyridyl*-3 : 5 : 3′ : 5′-*tetracarboxylate*,

$$\mathrm{MeN}<\begin{array}{l}\mathrm{CMe{:}C(CO_2Et)}\\ \mathrm{CMe{:}C(CO_2Et)}\end{array}>\mathrm{CMe{\cdot}MeC}<\begin{array}{l}\mathrm{C(CO_2Et){:}CMe}\\ \mathrm{C(CO_2Et){:}CMe}\end{array}>\mathrm{NMe},$$

pale yellow, lustrous needles, m. p. 80—82°, is prepared in 90—100% yield by the action of sodium amalgam on an aqueous solution of ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate methosulphate (cf. Mumm and Hingst, this vol., i, 83) in an atmosphere of carbon dioxide. When heated above its m. p. in an atmosphere of hydrogen, it is transformed into equivalent amounts of ethyl 1 : 2 : 4 : 6-tetramethyldihydropyridine-3 : 5-dicarboxylate and ethyl trimethylmethylenedihydropyridine-3 : 5-dicarboxylate, m. p. 72—73° (cf. Mumm and Hingst, *loc. cit.*); a similar "disproportionation" is observed under the influence of dilute hydrochloric acid. The dipyridyl compound (1 mol.) reacts with iodine (2 atoms) in alcoholic solution in the absence of air to give ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate methiodide. As intermediate or by-products, the *periodides*, $C_{14}H_{19}O_4N,MeI,I_2$, m. p. 102—103°, and $C_{14}H_{19}O_4N,MeI,I$, m. p. 114°, are observed. These substances can also be prepared from ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate and iodine in alcoholic solution; they are bimolecular. The dipyridyl compound when dissolved in benzene absorbs oxygen very rapidly, giving ethyl trimethylmethylenedihydropyridine-3 : 5-dicarboxylate, mixed with small amounts of ethyl 1 : 2 : 4 : 6-tetramethyldihydropyridine-3 : 5-dicarboxylate. It is readily hydrogenated in alcoholic solution in the presence of colloidal palladium to the unsymmetrical ethyl 1 : 2 : 4 : 6-tetramethyldihydropyridine-3 : 5-dicarboxylate, b. p. 145—152°/0·3 mm. (cf. Mumm and Hingst, *loc. cit.*). The latter compound is most sharply differentiated from its isomeride, m. p. 85°, by its behaviour towards hydrogen in the presence of spongy platinum and glacial acetic acid, whereby it is converted solely into ethyl 1 : 2 : 4 : 6-tetramethyltetrahydropyridine-3 : 5-dicarboxylate (*picrate*, yellow rhombohedra, m. p. 130—131°); the solid isomeride is more slowly hydrogenated, but is ultimately transformed into *ethyl* 1 : 2 : 4 : 6-*tetramethylhexahydropyridine*-3 : 5-*dicarboxylate*, a pale yellow liquid, b. p. 162—164°/11 mm. (*picrate*, m. p. 153°; *hydrochloride*, m. p. 66°; *hydrobromide*, m. p. 48°; *additive* compound with mercuric chloride, m. p. 147°). The tetrahydro ester is more conveniently prepared by the catalytic hydrogenation of ethyl 2 : 4 : 6-trimethylpyridine-3 : 5-dicarboxylate methosulphate, whereby the hexahydro derivative is also produced in small amount (cf. Neuhaus, *Diss.* Kiel, 1923).

H. W.

isoIndigotin. C. W. Hansen (*Ann. Chim.*, 1924, [x], 1, 94—134).—*iso*Indogenides, formed by condensation of *o*- and *p*-chloroaldehydes and an *o*-sulphonated aldehyde with oxindole, were prepared (cf. Wahl and Bagard, A., 1909, i, 735; Stollé, A., 1914, i, 992; Martinet and Dornier, A., 1921, i, 516). The chloro derivatives have been described independently by Neber and Röcker (A., 1923, i, 945); *sodium benzylideneoxindole-2-sulphonate* forms pale yellow crystals.

*iso*Indogenides exhibit slight tinctorial properties. The leuco-compound obtained by reduction of indine (Wahl and Hansen, A., 1923, i, 607) yields from concentrated alkaline solution a *tetra-benzoyl* derivative, m. p. 209°, which indicates that under the conditions specified the leuco-compound exists wholly or in part as  $C_6H_4<\begin{smallmatrix}-C\\NH\end{smallmatrix}>C\cdot OH\ OH\cdot C<\begin{smallmatrix}C-\\NH\end{smallmatrix}>C_6H_4$. Reduction of indine by means of zinc and acetic acid in presence of sodium acetate affords *diacetyl-leuco*iso*indigotin*, colourless crystals, m. p. 220°, isomeric with the diacetyl-leucoindigo described by Liebermann (A., 1888, 492). Disulphoisatide may be converted directly into indine by the action of ammonia in its alcoholic solution.

The paper contains a more detailed account of work already published on disulphoisatide, isatin, etc. (Wahl and Hansen, this vol., i, 322; cf. Dornier and Martinet, A., 1923, i, 852).

H. J. E.

Constitution of Salipyrine. S. Bodforss and A. Guthe (*Ber.*, 1924, **57**, [*B*], 842—846).—Although salipyrine is usually represented as antipyrine salicylate, it may possibly be an additive compound, *e.g.*, $CO_2H\cdot C_6H_4\cdot O...H...C_{11}H_{12}ON_2$. Antipyrine is a very weak base ($k=2\cdot8\times10^{-13}$), its salts in dilute solution being considerably hydrolysed. Aqueous or alcoholic solutions of salipyrine show only the reactions of its components. The alteration of *E.M.F.* produced by the addition of salipyrine to a cell containing a suspension of silver salicylate in saturated salicylic acid against a standard calomel electrode has been determined in comparison with the effect produced by the addition of acids and bases, and from the results it is concluded that undissociated salipyrine consists of an additive complex corresponding with the above formula. The conductivity of solutions of antipyrine hydrochloride has been studied and additive compounds of antipyrine with the following phenols have been obtained: vanillin, *p*-cresol, nitroresorcinol, protocatechualdehyde, and *p*-hydroxybenzaldehyde. R. B.

Thallous Picrolonate. M. Giua (*Gazzetta*, 1924, **54**, 204—206).—Almost pure thallous carbonate is obtainable in good yield by passing dried air through 95% or absolute ethyl, propyl, *iso*butyl, or *iso*amyl alcohol containing in suspension thallium in powder or thin strips.

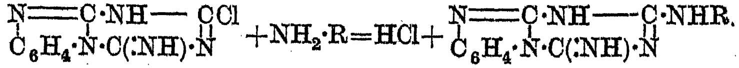
Thallous picrolonate, $C_{10}H_7O_5N_4Tl$, separates when a dilute acetic acid solution of picrolonic acid is added to a similar solution of the carbonate, and forms pale yellow needles, exploding above 300°.

T. H. P.

Quinazolines. XXXV. Stereoisomeric Styryl Derivatives of some 4-Quinazolone Alkiodides, and their Bearing upon the Problem of Photosensitising Dyes. M. T. Bogert and H. Clark (*J. Amer. Chem. Soc.*, 1924, **46**, 1294—1301).—Quaternary [illegible] salts could not be obtained from 2 : 4-dimethyl-, 2-styryl- [illegible] 2-phenyl-4-methyl-quinazolines; 2 : 4-dimethyl- [illegible] be condensed with aromatic aldehydes. The condensation of substituted 4-quinazolone alkiodides with *p*-dimethylaminobenzaldehyde yielded 2-*p*-dimethylaminostyryl-4-quinazolone alkiodides, the stereoisomeride obtained being dependent on whether piperidine or acetic anhydride was used as condensing agent, or, using the latter, on the conditions of experiment. The stable (purple) isomerides had higher m. p. than the (red) labile isomerides. The latter were converted into the stable forms by acetic anhydride at 120°, but the reverse change could not be effected. Both isomerides yielded the same monobromo-dibromides. The products have no value as dyes or photosensitisers. The following compounds are described. 2-p-*Dimethylaminostyryl*-4-*quinazolone methiodide*, reddish-purple needles, m. p. 265·7° (decomp.) with previous sublimation or darkening, or bright red needles, m. p. 214°; 2-p-*dimethylaminostyryl*-3-*methyl*-4-*quinazolone methiodide*, similar, m. p. 263·5° (decomp.) after subliming and darkening, or m. p. 216° (decomp.); *tribromo* derivative, orange needles, m. p. 178°; 2-p-*dimethylaminostyryl*-3-*methyl*-4-*quinazolone ethiodide*, similar, m. p. 264·7° (decomp.) after subliming and darkening, or m. p. 205·5°; 2-p-*dimethylaminostyryl*-3-*ethyl*-4-*quinazolone methiodide*, similar, m. p. 255° (decomp.) after subliming and darkening, or bright red needles with blue lustre, m. p. 212°; *tribromo* derivative, yellowish-orange needles, m. p. 152°.

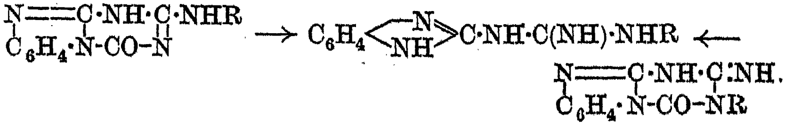
F. G. W.

Action of Cyanogen Halides on Phenylhydrazine. VIII. Exo-alkyl Derivatives of Melamine. G. PELLIZZARI (*Gazzetta*, 1924, **54**, 177—184).—*o*-Phenyleneammelyl chloride (cf. A., 1922, i, 585) reacts readily with primary amines to form melaminic bases having the alkyl group united to a nitrogen atom which does not form part of the nucleus:



$$\begin{array}{l}N{=\!=}C\cdot NH-CCl\\ C_6H_4\cdot N\cdot C(:NH)\cdot N\end{array} + NH_2\cdot R = HCl + \begin{array}{l}N{=\!=}C\cdot NH-C\cdot NHR.\\ C_6H_4\cdot N\cdot C(:NH)\cdot N\end{array}$$

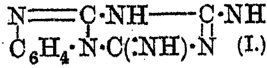
Such *exo*-alkylphenylenemelamines are isomeric with those obtained from the same amines and dicyanophenyleneguanidine (A., 1921, i, 620). Phenyleneammelyl chloride reacts also with secondary amines; with methylaniline, *e.g.*, it gives phenyl-*exo*-phenylenemethylmelamine (a white, crystalline powder, not melting at 300°), which is formed also by direct addition of methylaniline to dicyanophenyleneguanidine. Phenyleneammelyl chloride acts also on ammonia, giving a compound identical with that formed by direct addition of ammonia to phenyleneguanidine. When heated with hydrochloric acid, the *exo*-alkylphenylenemelamines behave like their isomerides, giving the corresponding ammelines. Treatment of the *exo*-ammelines thus formed with hot potassium hydroxide solution affords a single substituted diguanide, even from a pair of isomeric compounds:



$$\begin{array}{l}N{=\!=}C\cdot NH\cdot C\cdot NHR\\ C_6H_4\cdot N-CO-N\end{array} \longrightarrow C_6H_4{<}{\scriptstyle N \atop NH}{>}C\cdot NH\cdot C(NH)\cdot NHR \longleftarrow \begin{array}{l}N{=\!=}C\cdot NH\cdot C:NH.\\ C_6H_4\cdot N-CO-NR\end{array}$$

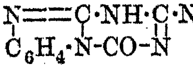
This result confirms the scheme given for the addition of hydrogen chloride to αβ-dicyano-*o*-phenyleneguanidine (A., 1922, i, 585), since, if the chlorine atom were fixed in the other possible position, the subsequent reactions would yield different melamine, ammeline, and diguanide.

Phenyl-exo-*phenylenemelamine* (I) is basic and forms minute needles not melting at 300°.



$$\begin{array}{l} N{=\!=}C\cdot NH{-\!-}C\cdot NHPh \\ C_6H_4\cdot N\cdot C(:NH)\cdot N \end{array}$$

(I.)



$$\begin{array}{l} N{=\!=}C\cdot NH\cdot C\cdot NHPh \\ C_6H_4\cdot N\text{-}CO\text{-}N \end{array}$$

(II.)

Phenyl-exo-*phenyleneammeline* (II), forms a white powder with high m. p. (decomp.).

Phenyl-exo-*phenylenemethylammeline*, $C_{16}H_{13}ON_5$, forms a white, microcrystalline powder, exhibits both acid and basic properties, and forms a *hydrochloride* ($+H_2O$). o-*Phenyleneguanylphenylmethylguanidine*, $C_6H_4\!<\!\begin{smallmatrix}N\\NH\end{smallmatrix}\!>\!C\cdot NH\cdot C(NH)\cdot NMePh$, forms colourless, lustrous, flat needles, m. p. 163°. T. H. P.

Thiazoles. IV. The Synthesis of Benzthiazoles from *o*-Nitrochlorobenzene. M. T. Bogert and F. D. Snell (*J. Amer. Chem. Soc.*, 1924, **46**, 1308—1311).—*o*-Aminothiophenol is obtained as the zinc salt by reducing *o*-nitrophenyl disulphide with zinc dust in glacial acetic acid. A suspension of the zinc salt in aqueous ammonium hydroxide is oxidised by a current of air to *o*-aminophenyl disulphide. 2-Phenylbenzthiazole is obtained by boiling the zinc salt of *o*-aminothiophenol with benzoyl chloride, or *o*-benzoylaminophenyl disulphide (m. p. 142·6°) with tin and dilute hydrochloric acid (etc.). 2-p-*Nitrophenylbenzthiazole*, similarly obtained, forms nearly colourless needles, m. p. 231°, and when reduced gives the corresponding amino derivative, which is also obtained by the reduction of 2-p-*nitrobenzoylaminophenyl disulphide*, pale yellow prisms, m. p. 217° (decomp.). F. G. W.

Azoxy-esters. A. Pieroni and G. Giannini (*Gazzetta*, 1924, **54**, 162—177).—The authors have prepared various members of a new class of compounds of the formula $R\cdot N_2O\cdot CO_2Et$, in which R represents an aromatic residue, by treating the corresponding azo-esters with peracetic acid for a period of some months (cf. Angeli, A., 1917, i, 228, 417).

By treating ethyl chlorocarbonate with the phenylhydrazine in pyridine solution (cf. Busch and Heinrichs, A., 1900, i, 314) almost quantitative yields may be obtained of ethyl phenylhydrazinecarboxylate (cf. Widman, A., 1895, i, 603) and of its *p*-chloro- and *p*-bromo-derivatives. Oxidation of these hydrazine compounds by means of potassium permanganate in acetic acid solution yields the corresponding azo-esters as deep red liquids of high density, which increases with the atomic weight of the substituent halogen. In presence of alkali, these azo-esters react with aldehydes thus: [illegible] $CO_2Et+2KOH=Et\cdot OH+K_2CO_3+NR{:}NH$ and $NR{:}NH+$ [illegible] COR, these reactions being strictly analogous [illegible] with the azocarbonamides (cf. Angeli, A. 1917, i, 228) and with the azoxy-esters (*vide infra*), from which normal diazotates are thus formed.

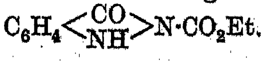
Treatment of the azo-esters in alcoholic solution with alcoholic potassium hydroxide results in the immediate separation of the potassium salts of the azocarboxylic acids, previously obtained from the azocarbonamides only by more or less complicated treatment (cf. Widman, *loc. cit.*; Thiele, A., 1896, i, 94). The corresponding silver and lead salts, prepared from the potassium salts by double decomposition, immediately decompose with copious liberation of nitrogen.

The azoxy-esters are dense, pale yellow, oily liquids, which in the light become brown, probably owing to the occurrence of a transformation similar to that taking place with azoxybenzene, $\mathrm{O{:}NPh\cdot NPh \longrightarrow OH\cdot C_6H_4\cdot N{:}NPh}$. Since the azoxy-esters are indifferent to the halogens, the constitution $\mathrm{O{:}NR{:}N\cdot CO_2Et}$ must be attributed to them. Just as was found with phenylazocarbonamide, the other isomeride is not formed under the conditions of oxidation employed, probably owing to the influence of the negative carbonyl group attached to the nitrogen atom.

When treated with alkali, the azoxy-esters undergo decomposition analogous to that shown by the azo derivatives, giving a normal diazotate, $\mathrm{O{:}NR{:}NH}$ (cf. Angeli, *loc. cit.*), which is unstable and decomposes, with formation of ammonia and a nitro derivative: $\mathrm{O{:}NPh{:}NH + H_2O = NH_3 + Ph\cdot NO_2}$.

When the oxidation of the azo-esters by peracetic acid is carried out at 50—60°, the azoxy-esters formed are accompanied by (1) the corresponding azoxybenzenes, which are probably due to the reaction $\mathrm{O{:}NR{:}N\cdot CO_2Et + NR{:}N\cdot CO_2Et \longrightarrow O{:}NR{:}NR}$, but may result from the oxidation of the azobenzenes formed as intermediate products; (2) chloro- or bromo-benzoic acid, the origin of which is as yet uncertain.

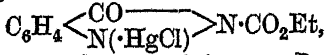
By a procedure analogous to that followed for the preparation of the hydrazo-esters, attempts have been made to obtain from the acid $\mathrm{CO_2H\cdot C_6H_4\cdot NH\cdot NH_2}$ the hydrazo-ester, $\mathrm{CO_2H\cdot C_6H_4\cdot NH\cdot NH\cdot CO_2Et}$, but the resulting compound contains a mol. of water less than the latter and is regarded as ethyl *o*-hydrazinobenzoylcarboxylate,



$\mathrm{C_6H_4{<}{\overset{CO}{\underset{NH}{}}}{>}N\cdot CO_2Et}$. *Ethyl phenylhydrazinocarboxylate*, $\mathrm{NHPh\cdot NH\cdot CO_2Et}$, forms white crystals, m. p. 85°; *ethyl* p-*chlorophenylhydrazinocarboxylate*, white needles, m. p. 92—93°, and *ethyl* p-*bromophenylhydrazinocarboxylate*, white needles, m. p. 110—111°; all these esters colour slightly in the air and light.

Ethyl benzeneazocarboxylate, $\mathrm{NPh{:}N\cdot CO_2Et}$, gives the iodoform reaction in methyl-alcoholic solution. *Ethyl* p-*chloro*- and p-*bromobenzeneazocarboxylates* show the same reaction. The three corresponding *potassium* salts form golden-yellow leaflets. *Ethyl benzeneazoxycarboxylate*, $\mathrm{O{:}NPh{:}N\cdot CO_2Et}$, was obtained as a slightly impure, straw-yellow oil and gives the iodoform reaction in methyl-alcoholic solution. *Ethyl* p-*chloro*- and p-*bromo-benzeneazoxycarboxylates* were not obtained sufficiently pure for analysis.

Ethyl o-*hydrazinobenzoylcarboxylate* has m. p. 194°. The *silver* derivative, $C_6H_4<{CO-\atop NAg}>N\cdot CO_2Et$, and the corresponding *mercurous* compound form colloidal solutions and gradually decompose when separated as hydrogels. The *mercurichloride*,


$$C_6H_4<{CO\text{———}\atop N(\cdot HgCl)}>N\cdot CO_2Et,$$

forms a microcrystalline, white precipitate. *Potassium* o-*hydrazinobenzoylcarboxylate*, which was not obtained pure, instantly reduces ammoniacal silver nitrate solution. T. H. P.

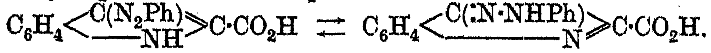
Azoxyamides and Pyrroles. A. Pieroni (*Gazzetta*, 1924, **54**, 157—161).—Like phenyldiazonium chloride (cf. Fischer and Hepp, A., 1886, 1041; Plancher and Soncini, A., 1903, i, 449), azoxyamides react with pyrrole and a number of its derivatives, yielding azo compounds. This reaction is effected best by *p*-bromo- and *p*-chloro-phenylazoxycarbonamides, which in an alkaline medium react in the usual way:

$$O\colon NR\colon N\cdot CO\cdot NH_2 \longrightarrow O\colon NR\colon N\cdot CO_2H \longrightarrow O\colon NR\colon NH,$$

coupling with the pyrrole then following. A similar reaction takes place between phenylazoxycarbonamides and indole, the azo group entering in the 3-position of the pyrrole nucleus.

2 : 2′-*Bis*-p-*bromobenzeneazopyrrole*, $C_{16}H_{11}N_5Br_2$, forms deep red crystals with copper reflection, m. p. 208°. p-*Bromobenzeneazoacetylpyrrole*, $C_{12}H_{10}ON_3Br$, crystallises in yellow laminæ, m. p. 168°. 2 : 5-*Dimethyl*-3-*benzeneazopyrrole* forms an orange-yellow, crystalline powder, m. p. 134°; 2 : 4-*dimethyl*-3-p-*bromobenzeneazopyrrole* has m. p. 152°. 3-p-*Bromobenzeneazoindole* crystallises in golden-yellow scales, m. p. 170°, and 3-*benzeneazoindole* in yellow crystals, m. p. 135°.

3-*Benzeneazoindole*-2-*carboxylic acid*, $C_{15}H_{11}O_2N_3$, obtained from sodium indole-2-carboxylate and benzeneazocarbonamide in methyl-alcoholic solution containing potassium methoxide, forms deep red, lustrous needles, m. p. 216° (decomp.). Its yellow solution in dilute alkali gives a precipitate of the red form on addition of mineral acid; its acetic acid solution is also red; it is therefore probably capable of the transposition:


$$C_6H_4<{C(N_2Ph)\atop \text{———}NH}>C\cdot CO_2H \rightleftarrows C_6H_4<{C(\colon N\cdot NHPh)\atop \text{————}N}>C\cdot CO_2H.$$

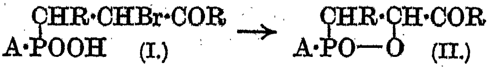
The product obtained under similar conditions from indole-3-carboxylic acid loses carbon dioxide, forming 3-benzeneazoindole (*vide supra*); if, with the same acid, *p*-bromophenylazoxycarbonamide is used, 3-*p*-bromobenzeneazoindole, m. p. 170°, is obtained.

2-*Methyl*-3-p-*chlorobenzeneazoindole*, $C_{15}H_{12}N_3Cl$, forms yellow needles, m. p. 168°. T. H. P.

Reduction of Nitronaphthalenes. II. β-Nitronaphthalene. W. M. Cumming and G. S. Ferrier (*J. Chem. Soc.*, 1924, **125**, 1108—1111; cf. T., 1923, **123**, 2466).—The reduction of 2-nitronaphthalene with zinc dust and alcoholic ammonium chloride yields [illegible] m. p. 164° (cf. Meisenheimer and Witte, [illegible] 2 : 2′-azonaphthalene. Further reduction undoubtedly occurs, giving hydrazonaphthalene; this at once undergoes atmospheric oxidation to 2 : 2′-azonaphthalene, or in absence of air, benzidine transformation to 2 : 2′-diamino-1 : 1′-dinaphthyl. 2 : 2′-Azonaphthalene is stable in air, but on oxidation with perhydrol in acetic acid yields 2 : 2′-azoxynaphthalene. Exposure to light in alcoholic solution converts 2 : 2′-azoxynaphthalene into a red *isomeride*, m. p. 162°, which, from a comparison of its absorption spectrum with that of 2-naphthaleneazo-2-naphthol, is considered to be a hydroxyazo compound (cf. Baudisch and Fürst, A., 1913, ii, 39). R. B.

Metallic Compounds of Dibenzoylhydrazide. A. Benrath (*J. pr. Chem.*, 1924, [ii], **107**, 211—224; cf. A., 1904, i, 935).—The solubility of dibenzoylhydrazide in water is 4·7 mg. per 100 c.c. at 17°. That of the monosodium derivative is 0·346 g./100 c.c. This salt is hydrolysed to the extent of 14% in aqueous solution and dibenzoylhydrazide is precipitated. The hydrolysis, therefore, is independent of the dilution; addition of sodium hydroxide lessens the hydrolysis but also decreases the solubility. Neutral salts, *e.g.*, sodium chloride, nitrate, or sulphate, likewise depress the solubility. The same behaviour is shown by the potassium salt; its solubility is 0·447 g./100 c.c. and it is hydrolysed 13·1%. The *lithium* salt, yellow crystals, has solubility 0·08 g./100 c.c. and 15·4% is hydrolysed. The *rubidium, cæsium, magnesium, calcium, barium, silver, thallium, copper, cobalt, nickel, zinc, cadmium,* and *manganese* salts are described, all being obtained by precipitation or double decomposition in an appropriate solvent. A third *lead* compound, $C_{14}H_{10}O_2N_2Pb$, a yellow powder, and two *mercury* derivatives, $[C_{14}H_{10}O_2N_2]_2Hg$ and $C_{14}H_{10}O_2N_2Hg,HgCl_2$, are also described. Dibenzoylhydrazide combines with metallic sodium in boiling toluene solution to a *disodium* compound, presumably CPh(ONa)⁚N·N⁚CPh(ONa), a yellow substance. W. A. S.

Mechanism of the Decomposition of β-Bromophosphinic Acids in Alkaline Solution. J. B. Conant and E. L. Jackson (*J. Amer. Chem. Soc.*, 1924, **46**, 1003—1018; cf. A., 1923, i, 69).—Certain β-bromophosphinic acids of the type (I) are quantitatively decomposed in aqueous alkaline solution. It was thought that an inner ester analogous to a β-lactone (a β-"phostone") (II) might be formed as an intermediate product:



$$\underset{\text{A·POOH}}{\text{CHR·CHBr·COR}}\ (\text{I.}) \longrightarrow \underset{\text{A·PO—O}}{\text{CHR·CH·COR}}\ (\text{II.})$$

(R=Aryl; A=·OH, Ph· or PHO·).

Attempts to prepare such β-phostones were unsuccessful. β-p-*Chlorobenzoyl-α-phenylethylphosphinic acid*, colourless crystals with 1 mol. of water, m. p. 112—114°, was prepared by the action of phosphorus trichloride on *p*-chlorophenyl styryl ketone in glacial acetic acid. The β-*bromo* derivative, m. p. 204°, obtained by bromination in chloroform solution, was difficult to obtain pure. The *phenyl* ester, $C_6H_4Cl·CO·CH_2·CHPh·PO(OPh)_2$, obtained by the action of phenol and thionyl chloride on the acid, formed crystals, m. p. 109°. Partial hydrolysis of the latter yielded the *phenyl* *hydrogen* ester, crystals, m. p. 180°. The β-*bromo* derivative of the phenyl ester had m. p. 127—129°. The β-*bromo* derivative of the phenyl hydrogen ester forms two *isomerides*, one, difficultly soluble in 5% sodium hydrogen carbonate, m. p. 195—196°, the other readily soluble, m. p. 150—151°. Both isomerides were decomposed by cold dilute sodium hydroxide with formation of *p*-chlorophenyl styryl ketone, showing them to be stereoisomerides. They were soluble in aqueous sodium carbonate without decomposition. It was not found possible by warming to eliminate the bromine atom (with β-phostone formation) without also splitting off the phosphinic group. Experiments carried out in "buffer" solutions of various alkalinities showed that the rate of decomposition was a function of the hydroxyl-ion concentration. This together with other evidence excludes β-phostone formation as an intermediate step in the decomposition of β-bromophosphinic acids. To obtain the corresponding methyl esters as crystallisable products with satisfactory yields, it was necessary to use a Carius tube. *Methyl hydrogen* β-p-*chlorobenzoyl-α-phenylethylphosphinate*, m. p. 152—153°, is obtained in 65—74% of the theoretical yield. It is accompanied by *methyl* β-p-*chlorobenzoyl-α-phenylethylphosphinate*, m. p. 123—124°. They are separated by means of sodium carbonate solution, in which only the former is soluble. The β-*bromo* derivative of the monomethyl ester is difficult to obtain pure (yield 25% of theory, m. p. 163—164°). It dissolves readily in sodium hydroxide with loss of the bromine atom. Its rate of decomposition was studied. The chief decomposition product was a monomethyl ester of either an unsaturated or a hydroxy-phosphinic acid. It is suggested that the first step in the decomposition of the β-bromophosphinic acids is the interaction of the organic molecule and the hydroxyl ion to form an unstable ionised hydroxyl compound. The further decomposition may take place in various ways corresponding with the several products obtained by the action of alkalis on different types of bromophosphinic acids. A. C.

Complex Boric Acid Compounds and the Optically Active Boron Atom. J. BÖESEKEN and J. MEULENHOFF (*Proc. K. Akad. Wetensch.*, 1924, **27**, 174—177).—The ammonium, aniline, *p*-chloroaniline, dimethylaniline, and pyridine salts of the dipyrocatechol–boric acid compound (cf. A., 1923, i, 557; ii, 406) have the composition $[B(O_2C_6H_4)_2]M$ or $[B(O_2C_6H_4)_2]H,NH_2R$, and form anhydrous crystals; the ammonium salt appears to volatilise unchanged. The free acid has the composition $[B(O_2C_6H_4)_2]H$. The aniline and pyridine salts of the dipyrogallol–boric acid compound have also been prepared, and likewise the potassium, ammonium, and aniline salts of the di-(3-nitropyrocatechol) and the di-(4-nitropyrocatechol) compounds, these having the constitution $[B(O_2C_6H_3\cdot NO_2)_2]R$ and forming anhydrous crystals.

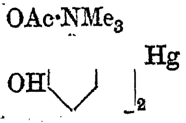
The salicylic acid–boric acid compound forms anhydrous aniline, [illegible] potassium, sodium, and silver salts, $[B(O_2COC_6H_4)_2]R$, [illegible] salt contains 1 mol., and the zinc, copper, [illegible] nickel, magnesium, and calcium salts 10 mols.

of water of crystallisation. The asymmetry of the anion is shown by the fact that the strychnine salt is separable into dextro- and lævo-rotatory components. T. H. P.

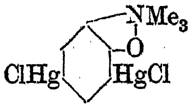
Stable Partial-valency Compounds of Triphenylboron, a Contribution to the Problem of the Valency of Boron. E. Krause (*Ber.*, 1924, 57, [*B*], 813—818).—Triphenylboron (cf. Krause and Nitsche, A., 1922, i, 694) unites readily with ammonia and with aromatic amines to form well-crystallised additive compounds stable to atmospheric oxygen; they contain 1 mol. of base, the boron having therefore the co-ordination number 4. The stability of the compounds is attributed in large part to steric effects, and also to a species of salt formation due to the acidifying effect of the phenyl groups. The following *compounds*, all of which form colourless crystals, were prepared by adding the requisite amine to triphenylboron in ethereal solution and have the general formula, Ph_3B,R (R=base): $R=NH_3$, m. p. above 212° (decomp.); $R=NH_2Me$, m. p. 208—209° (decomp. 210—211°); $R=NH_2Et$, m. p. 166—168°, decomp. above 200°; $R=NH_2Pr^{\alpha}$, m. p. 101—102°, decomp. above 180°; $R=NHMe_2$, m. p. 186—187°, decomp. 187—200°; $R=NMe_3$, m. p. 135—137°; $R=NH_2Ph$, m. p. 138—140° (decomp.). *Additive products* were obtained (not crystalline) with *ethyl*- and *diethyl-aniline*. R=*pyridine*, decomp. above 214°; R=*quinoline*, m. p. 160—170° (decomp.); R=*quinaldine*, m. p. 110—112° (decomp.); R=*piperidine*, m. p. 213—214°, decomp. above 216°; R=*phenylhydrazine*, $Ph_3B,Ph{\cdot}NH{\cdot}NH_2$, m. p. 138—140°; it is not stable in air indefinitely. Diphenylamine does not combine with triphenylboron. F. A. M.

Factors affecting the Stability of Mercurials and the Mercurisation of Substituted Phenylammonium Salts. M. S. Kharasch and L. Chalkley, jun. (*J. Amer. Chem. Soc.*, 1924, 46, 1211—1223).—Certain mercuri-organic compounds form a suitable means for testing the hypothesis that the comparative non-labilisation of a chlorine atom, *ortho* or *para* to one or two negative groups (as compared with a similarly situated bromine or iodine atom), may be due to intramolecular oxidation-reduction between the chlorine and carbon atoms, since the grouping –HgX undoubtedly remains positive, and any intramolecular oxidation-reduction is accompanied by the immediate separation of metallic mercury. 3-*Dimethylamino*-6-*acetoxymercuriphenol*, from mercuric acetate and *m*-dimethylaminophenol, in alcoholic solution, forms dirty yellow crystals decomposing with liberation of metallic mercury on storing for 10—14 days. It melts at 100—110° (decomp., with formation of a pink dye). On methylation it affords 3-*dimethylamino*-6-*acetoxymercurianisole hydrochloride*, faintly pink, leaf-like crystals, m. p. 140—150°, decomp. at 190°, to give a pink, fluorescent dye. On boiling a glacial acetic acid solution of mercuric acetate and *m*-dimethylaminophenol, metallic mercury is precipitated, and a mercury-free, pink dye is formed, the *base* of which, $C_{18}H_{22}O_2N_2$, is precipitated by ammonia.

3-*Dimethylamino*-6-*acetoxymercuriphenyl acetate*, similarly prepared from *m*-dimethylaminophenyl acetate, forms colourless crystals, m. p. 110°, which blacken on storing. 4 : 6-*Diacetoxymercuriresorcinoldimethyl ether*, similarly prepared, forms white, feathery crystals, m. p. 218—220°. *Mercuri-bis*-m-*hydroxyphenyltrimethylammonium acetate* (annexed formula), obtained by the action of mercuric acetate on *m*-hydroxyphenyltrimethylammonium hydroxide, forms a hygroscopic, white powder, m. p. 116—117° (decomp.). On treatment with mercuric chloride in 60% alcohol, it affords m-*hydroxychloromercuriphenyltrimethylammonium anhydride*, $ClHg\cdot C_6H_3(NMe_3O)$, as a white solid, m. p. 130—150° (decomp.). 4-*Hydroxy*-3 : 5-*diacetoxymercuriphenyltrimethylammonium acetate* forms colourless needles, m. p. 155—160° (decomp.), which are stable when dry. 4-*Hydroxy*-3-*chloromercuriphenyltrimethylammonium acetate* is obtained from the mother-liquors of the last compound by treatment with sodium chloride, as small, slightly brown needles, m. p. 155—160° (decomp.).



2-*Hydroxy*-3 : 5-*dichloromercuriphenyltrimethylammonium anhydride* (annexed formula), obtained by treating the product of the reaction between *o*-hydroxyphenyltrimethylammonium hydroxide and mercuric acetate with sodium chloride, forms a white, amorphous solid, m. p. 215—220° (decomp.), after turning violet at 200—210°.



m-Aminophenyltrimethylammonium chloride hydrochloride, $C_6H_4(NMe_3Cl)\cdot NH_2,HCl$, obtained by heating *m*-nitroaniline hydrobromide with methyl alcohol under pressure at 90—100° and reducing the product, forms pale yellow needles, m. p. 190—200° (decomp.). On treatment with silver hydroxide, it yields the base without decomposition, and this reacts with mercuric acetate with formation of 3-*amino*-4 : 6-*dichloromercuriphenyltrimethylammonium acetate*, colourless crystals, m. p. 200° (decomp.). The times required for blackening to commence when the above compounds are treated with hydrogen sulphide in pyridine or pyridine-water solution are given, and the bearing of these results on the two-stage mercurisation hypothesis of Kharasch and Jacobsohn (A., 1922, i, 189) is discussed. F. G. W.

Hydroferrocyanides and Hydroferricyanides of the Organic Bases. III. W. M. Cumming (*J. Chem. Soc.*, 1924, **125**, 1106—1108).—The hydroferrocyanides obtained from a number of organic bases by precipitation in alcoholic solution are described (cf. T., 1922, **121**, 1287; 1923, **123**, 2457).

Hydroferricyanides have also been produced in acid and neutral alcoholic solutions. Even at —20°, the salts of primary bases oxidise very rapidly. Most secondary bases only give pure salts at low temperatures, whereas tertiary bases yield well-defined salts at the ordinary temperature. The formation of a hydroferri- [illegible] hindered by the presence of an acidic substituent in the [illegible] the case of *p*-bromo- and *p*-nitroso-dimethylaniline; such substituents in a primary amine appear to prevent oxidation. The hydroferricyanides form well-defined crystals which are more highly coloured and more stable than the corresponding hydroferrocyanides previously described (T., 1922, **121**, 1288). The constitution of the salts depends on the acidity of the solution, except in the case of methylaniline. C. J. S.

Halogenated Proteins. II. Bromopeptone. A. J. J. VANDEVELDE (*Rec. trav. chim.*, 1924, **43**, 326—328).—Witte's peptone reacts with bromine in carbon tetrachloride solution, forming *bromopeptone A*, a hygroscopic, yellow powder having an irritating odour and containing 37·55% of bromine. When treated with hot alkali hydroxide solution, it loses bromine corresponding with 33·29% of its weight. At 100°, bromopeptone A undergoes partial decomposition, forming the hygroscopic *bromopeptone C*, containing 30·83% of bromine, and losing 25·61% when warmed with potassium hydroxide solution. Bromopeptone A can be separated into its constituents in the same way as the original peptone; the quantity of albumoses is found to have diminished and the amino acids increased. The precipitates obtained from a solution of the bromopeptone with zinc sulphate or with phosphotungstic acid contain very little bromine (cf. this vol., i, 678).
E. H. R.

Nitration of Proteins. I. and II. F. LIEBEN (*Biochem. Z.*, 1924, **145**, 535—554; 555—559).—I. From a quantitative study of the course of nitration of silk-fibrin, casein, and blood-fibrin with concentrations of nitric acid varying from 5 to 60%, it is concluded that in each case the process consists in the formation of the mononitro derivatives of the tyrosine residues, and if tryptophan is also present, as in casein and blood-fibrin, this amino-acid also gives rise to a mononitro derivatve. Nitrofibroin and nitrocasein are reduced to colourless products by hydrogen and sodium hyposulphite in the presence of sodium carbonate. The amino nitrogen of the reduced products determined by Van Slyke's method is the same as that of the nitroproteins (a new amino-protein is therefore not formed on reduction), and slightly greater than that of the original protein, an increase which is ascribed to degradation during nitration.

II. The quantitative course of the nitration of serum-albumin, serum-globulin, lactalbumin, edestin, gliadin, and keratin is in agreement with the supposition (cf. I.) that the mononitro derivatives of the tyrosine and tryptophan present in these proteins are formed. J. P.

Biochemistry.

Blood as a Physico-chemical System. II. L. J. Henderson, A. V. Bock, H. Field, and J. L. Stoddard (*J. Biol. Chem.*, 1924, **59**, 379—431).—A complete description of the changes known to occur in blood during the respiratory cycle and of the physico-chemical system which determines them is given. It has been shown (cf. A., 1921, i, 473) that all external changes in oxygen or carbon dioxide tension are invariably accompanied in blood, not only by changes in free and combined oxygen and carbonic acid concentrations, but also by changes in hydrogen-ion concentration and in the distribution of chlorides between cells and plasma. This study of the physico-chemical system was incomplete, since the movement of water between cells and plasma was left out of account. This factor is now further investigated and it appears that the theory concerning water and chloride distribution as a function of buffer actions of proteins, of alkali reserve, and of osmotic pressure (A., 1909, ii, 157) is valid. All the known phenomena of the respiratory cycle in blood have been described with a good approach to accuracy with the following seven variables: free oxygen, total oxygen, free CO_2, total CO_2, p_H of the serum, the volume of the corpuscles, and the ratio of the concentrations of anions within and without the cell. D. R. N.

Oxygen and Carbon Dioxide Dissociation Curves of Human Blood. A. V. Bock, H. Field, and G. S. Adair (*J. Biol. Chem.*, 1924, **59**, 353—378).—The oxygen dissociation curves for the blood of normal subjects at carbon dioxide tensions varying between 3 and 80 mm. do not conform to Hill's formula (*J. Physiol.*, 1910, **40**, 4). Carbon dioxide dissociation curves on fully reduced and fully oxygenated blood as well as the true plasma curves have also been studied. Both corpuscles and plasma transport carbon dioxide, the former carrying 40% of the total and the latter 60%.

D. R. N.

Chemistry of Hæmoglobin. II. Equilibrium between Oxygen and Hæmoglobin. R. M. Ferry (*J. Biol. Chem.*, 1924, **59**, 295—327).—The equilibrium between oxygen and hæmoglobin has been examined by a method based on a study by purely physical means of the gas phase in equilibrium with hæmoglobin and susceptible of considerable accuracy. A measured volume of hæmoglobin is brought into equilibrium with varying quantities of oxygen in an apparatus having a known volume, so arranged that a portion of the gas phase can be removed and measured without altering the equilibrium in the liquid phase and thus not only the amount of oxygen in the entire gas phase, but also its tension can be calculated through the application of gas laws. The difference between the quantity of oxygen introduced and that in the gas phase corresponds with the amount in combination with [illegible]

D. R. N.

Variations in the Acid–Base Balance of the Blood in Disease. V. C. Myers and L. E. Booher (*J. Biol. Chem.*, 1924, 59, 699—712).—A series of determinations of the p_H and the carbon dioxide content of the venous blood plasma of normal and diseased individuals was made. It was found that in pathological condition the p_H may be within normal limits whilst the carbon dioxide content is abnormal, and *vice versa*, so that the determination of one of these quantities alone is an insufficient index of the state of the acid–base balance. C. R. H.

Effect of Ether added *in vitro* on the Distribution of Carbon Dioxide and Chloride between Cells and Serum. J. H. Austin and H. C. Gram (*J. Biol. Chem.*, 1924, 59, 535—541).—Observations on the carbon dioxide and chloride content, the hydrogen-ion concentration, and the relative volume of cells and serum in blood equilibrated at a known tension of carbon dioxide, reveal no change in any of these quantities whether or no ether in anæsthetic concentration is present in the blood. C. R. H.

Changes in the Stability and Potential of Cell Suspensions. II. Potential of Erythrocytes. A. H. Eggerth (*J. Gen. Physiol.*, 1924, 6, 587—596).—When erythrocytes from human or sheep blood are washed with physiological salt solution and then suspended in solutions of p_H 5·2 or more acid, they become progressively more electropositive. This change is coincident with hæmolysis, and is, in fact, due to the escape of hæmoglobin from the cells, as in shown by the effect of adding hæmoglobin to a fresh suspension of cells. The isoelectric point of erythrocytes in the absence of salts or in the presence of salts with univalent ions is at p_H 4·7; in the presence of salts with bivalent anions it becomes more acid. C. R. H.

Agglutination of Red Blood Cells. J. H. Northrop and J. Freund (*J. Gen. Physiol.*, 1924, 6, 603—613).—The agglutination of unsensitised sheep erythrocytes by electrolytes usually occurs when the potential difference between cells and solution is reduced below 6 millivolts; in the case of sensitised cells, the corresponding critical potential difference is about 12 millivolts. It therefore appears that agglutination by immune serum is due to an increase in the critical potential difference and not to a lowering of the actual potential of the cells. C. R. H.

Coloration of so-called "Oxydasic" Granulations of Cells Obtained by Synthesis with Indophenol and Hydroxybenzidine. A. C. Hollande (*Compt. rend.*, 1924, 178, 1215—1217).—Human leucocytes which take up colouring matters derived from indophenol and hydroxybenzidine do so as a result of that type of dyeing which involves precipitation of the colour. The portions which become coloured are the granulations and also the liquid substances which are formed from or give rise to them. They are not dyed by phenylene-blue or toluylene-blue, and there appears to be no relation between existence of oxydase or peroxydase and power of colour-absorption. H. J. E.

Urea Content of Red Blood Cells. Z. Aszódi (*Biochem. Z.*, 1924, **146**, 343—348).—In the blood of normal individuals the urea is uniformly distributed between corpuscles and plasma, whilst in cases of kidney affections the plasma may contain rather more urea than the corpuscles (cf. Falta and Richter-Quittner, *ibid.*, **100**, 148; Andresen, *ibid.*, **116**, 266). J. P.

Cause of the Rapid Disappearance of Catalase in Blood Solutions. O. Steppuhn and A. Timofejewa (*Biochem. Z.*, 1924, **146**, 108—114).—From measurements of the "protease number" (Bach and Zubkova, A., 1922, i, 392) of dilute blood solutions in the presence of trypsin, it is concluded that the latter has no effect on the protease, as measured by the catalase activity, and that no evidence is forthcoming in support of the view that blood catalase is destroyed by proteases (cf. Wäntig and Steche, *Z. physiol. Chem.*, 1914, **93**, 228). The disappearance of catalase is associated with the presence of erythrocytes, and does not occur in serum. It is not affected by the presence of sodium oleate. In physiological salt solution, the catalase activity first falls rapidly, then rises to normal values. J. P.

Behaviour of the Lipoids of the Blood Immediately after Fat Ingestion in Normal and Diabetic Cases with and without the Administration of Insulin. H. U. Hartmann (*Biochem. Z.*, 1924, **146**, 307—317).—The lipoids of the blood are not affected by the ingestion of dextrose. One hour after the administration of 50 g. of butter and 20 g. of oatmeal to normal and diabetic subjects, a rise in the blood lipoids occurs, but these return to a normal level after 4 hours. The individual components of the lipoid fraction show irregular variations. In one case of diabetes (no acidosis), the blood lipoids were permanently above normal, chiefly due to an increase in neutral fat and cholesterol ester. In three out of four cases of diabetes, insulin slightly depressed the total lipoids of the blood, but no specific effect on any one component was observed. A previous injection of insulin has no effect on the increase of lipoids following the ingestion of butter and oatmeal, and the blood-sugar curve is independent of the lipoid curve. J. P.

Fatty Acids of Blood Plasma. II. Distribution of Unsaturated Acids. W. R. Bloor (*J. Biol. Chem.*, 1924, **59**, 543—556).—A fractionation of the total lipoids of blood plasma indicates that the greater part of the unsaturated fatty acids are present in the form of cholesterol esters; the iodine values of the acids from these esters show that they must include acids of a higher degree of unsaturation than oleic. C. R. H.

Detection of Higher Multiple Unsaturated Free Fatty Acids in Blood. A. von Szent-Györgyi.—(See ii, 508.)

Quantitative Determination of the Free Fatty Acids of [illegible] Szent-Györgyi and T. Tominaga.—(See

Uric Acid Content of the Serum and Spinal Fluid in Children. E. Lesné, Hasard, and Langle (*Compt. rend. Soc. Biol.*, 1923, **89**, 891—893; from *Chem. Zentr.*, 1924, i, 681).—In the blood-serum of children aged between 3 months and 12 years, the mean uric acid content was found to be 0·0035% as against 0·0049% in the case of the blood-serum of adults. The mean uric acid content of the spinal fluid of children was 0·0018%. In tubercular meningitis no appreciable increase in the uric acid content of the spinal fluid was observed. With meningococcal meningitis, on the other hand, there was a marked increase to 0·0038% of uric acid. G. W. R.

Nuclein Metabolism. II. Isolation of a Nucleotide from Human Blood. H. Jackson (*J. Biol. Chem.*, 1924, **59**, 529—534).—The precipitate obtained by treating a protein-free filtrate from blood with lead acetate in the presence of acetic acid yielded a substance which gave the reaction for pentoses and from which, after hydrolysis with dilute sulphuric acid, adenine was isolated as the picrate. C. R. H.

Diffusibility of the Calcium of Blood-serum through Collodion Membranes. Effect of Sodium Chloride and Changes in Hydrogen-ion Concentration. R. F. Loeb [with S. Steinberger] (*J. Gen. Physiol.*, 1924, **6**, 453—456).—Only 55—75% of the calcium present in serum is dialysable through collodion membranes against distilled water at p_H 7·4, but the whole of the calcium is dialysable against 0·8% sodium chloride solution of p_H 7·4, or against hydrochloric acid of p_H 2·5. W. O. K.

Action of Bicarbonate and Secondary Phosphate on the Dissociation of Calcium. H. Behrendt.—(See ii, 456.)

Accurate Determination of Calcium in Whole Blood. A. C. Alport.—(See ii, 500.)

Micro-determination of Methyl Alcohol in Blood. N. V. Bildsten.—(See ii, 506.)

Coagulation of Blood. J. Amar (*Compt. rend.*, 1924, **178**, 1628—1630; cf. this vol., ii, 144).—Further experiments show the bearing on the coagulation of blood of those physico-chemical factors which determine the coagulation of colloids by depressing the surface tension of the medium. Coagulation of blood is due to the disturbance of the equilibrium of its components resulting from a fall in the surface tension. This may be due to the action of a solid partition which is moistened by water, and to the standing of the blood, this causing separation of the components of the emulsion in the order of their densities, so that the solubilising salts of the supernatant liquor leave the corpuscles free to precipitate. Addition of salts, alcohols, or poisons capable of coagulating the proteins hastens the formation of the clot. Coagulation exhibits also an enzymic aspect, the diminution in the surface tension liberating the fibrin-coagulating enzyme of the leucocytes; that this is the case is shown by the observation that the production of filaments begins round the white corpuscles.

The view that sodium salts have anti-coagulating properties only because they precipitate the calcium salts is inaccurate, sodium carbonate, chloride, and phosphate being true anti-coagulants. Further, excess of calcium chloride exerts a toxic action on the leucocytes, shrivelling and coagulating their protoplasm and preventing the discharge of the fibrin enzyme and hence the coagulation of the blood; such effect is the opposite of that usually attributed to calcium chloride. T. H. P.

Lipolytic Theory of Immune Hæmolysis. R. Brinkman and A. von Szent-Györgyi (*Biochem. Z.*, 1924, **146**, 212—216).—Immune hæmolysis of blood by the addition of amboceptor and complement is not associated with liberation of higher fatty acids. After complete complement-fixation, the lipolytic activity of the serum is undiminished, and it is concluded that complement is not identical with blood lipase (cf. Olsen and Goette, *ibid.*, 1920, **112**, 188). Normal erythrocytes after reversal of hypotonic hæmolysis (*J. Physiol.*, 1923, **58**, 204) show immune hæmolysis, but reversal is not possible after the latter process. Amboceptor and complement are active in blood hæmolysed by hypotonic saline. J. P.

Formation of Porphyrin from Sulphur-Hæmoglobin. P. List (*Z. physiol. Chem.*, 1924, **135**, 95—107; cf. Schumm, A., 1923, i, 631).—The author has prepared porphyrins from blood treated with hydrogen sulphide (sulphur-hæmoglobin) by the action of hydrochloric acid. Weak acids, such as phosphoric and acetic acids, are also able to produce colouring matters of the porphyrin type. The products closely resemble the better known porphyrins in absorption spectra, but differ from them in being readily soluble in chloroform. E. M. C.

Determination of Hydrogen Ions in the Gastric Contents. J. F. McClendon (*J. Biol. Chem.*, 1924, **59**, 437—442).—A fairly accurate and rapid method is described for the determination of the p_H of the gastric juice based on the colorimetric determination of the percentage dissociation of quinaldine-red. D. R. N.

Polarimetric Observations on Solutions of Glucose after Contact with Intestinal Mucosa. H. V. Hume and W. Denis (*J. Biol. Chem.*, 1924, **59**, 457—464).—In order to prove the transitory formation of γ-glucose in glucose solutions after contact with intestinal mucosa, experimental technique other than that involving the use of the polarimeter will have to be employed (cf. A., 1920, i, 508, 648). Although this method gives unmistakable evidence of the existence of mutarotation, it could scarcely [illegible] formation of γ-glucose, as in some experiments [illegible] a decrease in the rotation are observed. D. R. N.

Inorganic Substances in Carbohydrate Metabolism. G. A. Harrop and E. M. Benedict (*J. Biol. Chem.*, 1924, **59**, 683—697).—During a period of active assimilation of carbohydrate there is a lessened excretion of phosphate; coincidently with this, there is a reduction of the concentration of inorganic phosphate in the blood-serum and an increase in its concentration in the muscle-tissue. These results are in favour of the view that inorganic phosphate is a necessary intermediate in the storage of carbohydrate as glycogen. C. R. H.

Formation and Origin of Acetaldehyde in the Intermediate Cellular Metabolism of Warm-blooded Animals. C. Neuberg and A. Gottschalk (*Biochem. Z.*, 1924, **146**, 164—184).—The presence of acetaldehyde—originating from glycogen—in the surviving cells of guinea pig liver pulp can be demonstrated by the use of calcium hydrogen sulphite, and the acetaldehyde may be determined quantitatively by alkalimetric titration using hydroxylamine sulphate (Sieber, *Chem.-Ztg.*, 1921, **45**, 349). The amount of acetaldehyde formed is increased by the addition of sugars and other related substances, and is greatly increased if insulin be added simultaneously. The activity in forming acetaldehyde diminishes in the following order: glycogen, *dl*-glyceraldehyde, zymophosphate, hexose monophosphate, dihydroxyacetone, glycollaldehyde, *d*-fructose, *d*-glucose, whilst from the following compounds the yields of aldehyde also diminished in the order: ethyl alcohol, alanine, *d*-mannitol, *dl*-glyceric acid, glycerol, and glycerophosphoric acid. J. P.

Separation and Identification of Acetaldehyde Formed in the Intermediary Metabolism of Surviving Cells of Warm-blooded Animals. C. Neuberg and A. Gottschalk (*Biochem. Z.*, 1924, **146**, 185—187).—The identity of the acetaldehyde obtained as the calcium sulphite compound in investigating the metabolism of surviving cells of the liver (cf. preceding abstract) is established by the isolation and analysis of the crystalline *p*-nitrophenylhydrazone (m. p. 128°). J. P.

Some Oxidation Processes of Normal and Cancer Tissue. A. Fleisch (*Biochem. J.*, 1924, **18**, 294—311).—Glutathione has the same effect with thermostable sarcoma residue as with thermostable muscle residue. Unwashed sarcoma tissue reduces methylene-blue more slowly than muscle. The total amount of oxygen taken up is greater for sarcoma tissue, although it shows a lower initial velocity of oxygen uptake than muscle. Hydrogen cyanide inhibits the oxygen uptake, but not the methylene-blue reduction of unwashed tissue in both cases. Citric acid accelerates the methylene-blue reduction of washed muscle, but not of washed sarcoma. Cyanide has no influence. Muscle as well as sarcoma oxidises citric acid in the Barcroft apparatus. This oxidation is not sensitive to hydrogen cyanide. The most favourable reaction for it is p_H 6·0. Glutamic acid is oxidised by washed muscle and sarcoma in presence of methylene-blue; lactic acid, on the other hand, is less actively oxidised by sarcoma than by muscle. Fumaric, maleic, and malic acids are not oxidised in this way by either tissue. Succinic acid is oxidised freely whether in the presence of methylene-blue or oxygen, and muscle is the more active of the two in this respect. The quantity of oxygen used corresponds with 1 atom of oxygen for 1 mol. of succinic acid. Whilst hydrogen cyanide has no effect on the methylene-blue reduction, the oxygen uptake by succinic acid is inhibited by it. The oxidation of succinic acid with oxygen can in the case of muscle be restored if methylene-blue is added to the system. This indirect oxidation of succinic acid induced by the methylene-blue occurs to a much less extent in the case of sarcoma. There is evidence that a "hydrogen transport factor" exists which is of importance for the transport of hydrogen to methylene-blue. The factor is distinct from "succinoxydase," and can be washed out. Its concentration is much smaller in sarcoma than in muscle-tissue. The mechanism of the aërobic oxidation of succinic acid is discussed. S. S. Z.

Biological Oxidation. I. Absorption of Oxygen by the System Linoleic Acid–SH Group. A. von Szent-Györgyi.—(See this vol., i, 708.)

Biological Oxidation. II. Mechanism and Significance of SH-Catalysis. A. von Szent-Györgyi.—(See this vol., i, 708.)

Effect of Exercise in Diabetes. I. H. E. Himwich, R. O. Loebel, and D. P. Barr (*J. Biol. Chem.*, 1924, 59, 265—293).—Following short periods of vigorous exercise in the diabetic, there are changes in acid–base equilibrium somewhat greater than in normal individuals doing a comparable amount of work, as is apparent from a reduction of CO_2 capacity, CO_2 tension, and alkalinity of arterial blood. There is a marked increase of lactic acid and the reduction of CO_2 capacity can be quantitatively accounted for by this increase. After exercise for short periods, no significant change in the concentration of acetone compounds could be observed. The accumulation of lactic acid in the blood of diabetics after exercise indicates that the conversion of carbohydrate into lactic acid is employed as the chemical mechanism of muscular contraction. D. R. N.

Mechanism of the Action of Insulin. The Carbohydrate Balance in Avitaminosis. A. Bickel and J. A. Collazo (*Deuts. med. Woch.*, 1923, 49, 1408—1410; from *Chem. Zentr.*, 1924, i, 685).—The liver and muscles of pigeons suffering from avitaminosis are practically free from glycogen and the blood-sugar is above normal. Insulin decreases the blood-sugar content and with repeated injections and subsequent administration of sugar recovery takes place. The liver and muscle contain glycogen [illegible] of insulin, whilst the content of fats and [illegible] blood falls. The effect of a single injection of insulin disappears after 24 hours. Insulin appears to facilitate the storage of glycogen. G. W. R.

Changes in the Ionic Content of the Blood after Administration of Insulin. H. STAUB, F. GÜNTHER, and R. FRÖHLICH (*Klin. Woch.*, 1923, **2**, 2337—2338; from *Chem. Zentr.*, 1924, i, 685).—After administration of large doses of insulin to normal dogs and to dogs suffering from diabetic coma, decrease of acidosis, increase of p_H, and increase of the content of sodium, potassium, calcium, and magnesium occur. A marked decrease in inorganic phosphorus in the blood is noted. G. W. R.

Cholesterol Synthesis in the Animal Body. H. BEUMER and F. LEHMANN (*Z. ges. Exp. Med.*, 1923, **37**, 274—280; from *Chem. Zentr.*, 1924, i, 684).—Newly-born dogs fed for 4 weeks on a diet poor in cholesterol, showed an increase in cholesterol in 4 weeks amounting to 20 times the amount of cholesterol administered in the food. The formation of cholesterol therefore probably takes place exclusively from constituents not found in the ether extract of the food substances. G. W. R.

Nitrogen Metabolism in Avitaminosis. J. A. COLLAZO (*Biochem. Z.*, 1924, **145**, 436—441).—In dogs, the urinary purine nitrogen, uric acid, allantoin, ammonia, and amino-acids increase slightly with progressive avitaminosis, but shortly before death they may fall. The variations in uric acid and allantoin are sometimes parallel, sometimes divergent. Urea shows a continuous diminution in avitaminosis, whilst the urinary phosphates are normal in the initial stages, but increase with decreasing body-weight during the late stages. The residual nitrogen of the blood may remain normal for some time, but has a slight tendency to increase. Blood urea behaves in a similar way, whilst the amino-acids of the blood show a slow increase, which becomes more marked in advanced avitaminosis. The increase in the residual nitrogen of the blood is conditioned more by the amino-acids than by urea. It is concluded that in avitaminosis nitrogen metabolism is not disturbed so quickly as carbohydrate and fat metabolism. J. P.

Amino-acids in Nutrition. VIII. Proline. B. SURE (*J. Biol. Chem.*, 1924, **59**, 577—586).—Rats show a marked increase in the gain in weight per gram of protein intake on the addition of proline to a diet composed of edestin together with cystine and lysine. This effect was not obtained with an equivalent amount of pyrrolidonecarboxylic acid. It is concluded that proline is essential for growth. C. R. H.

Synthesis of Amino-acids in the Animal Organism. III. Cystine. J. A. MULDOON, G. J. SHIPLE, and C. P. SHERWIN (*J. Biol. Chem.*, 1924, **59**, 675—681).—The fact that bromobenzene is detoxicated in the animal body by conjugation with cysteine, to form *p*-bromophenylmercapturic acid, was utilised to test the ability of the dog to synthesise cystine. It was found that only when cystine was fed was there a synthesis of *p*-bromophenylmercapturic acid; neither the cystine of the tissues of the animal itself nor sulphur in other forms in the diet could be utilised for this purpose. C. R. H.

Cystine Deficiency and Vitamin Content of the Lentil, (*Lens esculenta*). D. B. Jones and J. C. Murphy (*J. Biol. Chem.*, 1924, **59**, 243—253).—The proteins of the lentil, like those of beans, are inadequate for nutritive purposes because of their deficiency in cystine and are further characterised by a form of indigestibility which can be corrected by cooking, although the effect of cooking is much less marked in the case of the lentil than in that of other legumes. The vitamin-*A* and vitamin-*B* contents of lentils appear to be much higher than in most other seeds. D. R. N.

Metabolism of Sulphur. VII. Oxidation of Sulphur Compounds Related to Cystine in the Animal Organism. VIII. Behaviour of Thiophenol and Thiocresol in the Animal Organism. R. M. Hill and H. B. Lewis (*J. Biol. Chem.*, 1924, **59**, 557—567, 569—575).—VII.—After administration of the sodium salts of thiolactic and thioglycollic acid to rabbits, either subcutaneously or orally, practically all the sulphur is eliminated in the urine in the first day, 50—70% of it being in the form of inorganic sulphate. Under similar conditions, the sulphur of thiodiglycollic acid is excreted in the unoxidised form.

VIII.—Thiophenol and *p*-thiocresol when administered to rabbits are absorbed only to a small extent; the sulphur is excreted entirely in the unoxidised form.

The authors suggest that in order that a sulphur compound may be susceptible of oxidation in the animal body, the sulphur must be present in an aliphatic mercapto group, or must be able to be transformed into such a condition. C. R. H.

Experiments upon Vitamin-*A*. H. C. Sherman and M. M. Kramer (*J. Amer. Chem. Soc.*, 1924, **46**, 1055—1063).—Young rats (4 weeks) placed on a diet devoid of vitamin-*A*, but adequate in all other respects for healthy nutrition, showed very different growths and survival periods, depending on the food eaten previous to the experimental period. It is suggested that the stores of vitamin-*A* in the bodies of the animals experimented on seriously vitiate the value of much of the earlier work on this subject. Vitamin-*A* was shown to be stored at later ages, and the length of time adult animals can survive on a diet devoid of it, but otherwise adequate, also depends on the amount of this vitamin stored in the body and is an indication of the relative amounts contained in earlier diets. A. C.

Experimental Rickets in Rats on a Purified Synthetic Diet Deficient in Phosphorus and Fat-soluble Organic Factor. H. Goldblatt (*Biochem. J.*, 1924, **18**, 414—418).—The addition to a purified synthetic diet low in phosphorus and the fat-soluble organic factor of calcium carbonate in such an amount that the proportion of calcium to phosphorus was raised from 1 : 0·88 to 1 : 0·20 had the effect of changing the diet from a non-rickets-producing to a rickets-producing one. S. S. Z.

Remarks on Papers of W. R. Hess and K. Rohr, "The Action of Thermal Treatment of Dry Yeast, etc., and Avian Beriberi," and of Roelli, "The Activation of *in vitro* Respiration by Muscle Juice, etc." E. ABDERHALDEN (*Z. physiol Chem.*, 1924, **134**, 97—99; cf. *Z. physiol. Chem.*, 1923, **192**, 268, 284).—Polemical. W. O. K.

Necessary Conditions for Testing with the Reagent for Vitamin-*C*. (Answer to H. D. Kay and S. S. Zilva.) N. BEZSSONOFF (*Biochem. J.*, 1924, **18**, 384—386).—Polemical. S. S. Z.

Supposed Influence of Irradiated Air on Growth. T. A. WEBSTER and L. HILL (*Biochem. J.*, 1924, **18**, 340—346).—The authors cannot confirm Hume and Smith's results regarding the growth-promoting effects of irradiated air (cf. A., 1923, i, 728). S. S. Z.

Influence of Cell Salts on Intermediate Metabolism. K. TADENUMA (*Biochem. Z.*, 1924, **145**, 481—491).—Dogs kept on a diet containing only sodium chloride as salt component, but otherwise adequate, show a diminution in body-weight, an increase in the residual nitrogen of the blood, and in general an increase in the blood-sugar compared with similarly fed animals receiving an artificial cell salt mixture. The neutral fat of the blood has a slight tendency to increase. In dogs kept on an insufficient diet, substitution of sodium chloride for the salt mixture accentuates the disturbances in metabolism. In general, it is concluded that dogs receiving a diet of adequate calorie value but insufficient in salts exhibit symptoms similar to those of avitaminosis. J. P.

Presence of Silicon in Tissues. L. ISAACS.—(See ii, 499.)

Importance of Zinc in the Feeding of Animals. G. BERTRAND and B. BENZON (*Ann. Inst. Pasteur*, 1924, **38**, 405—419).—A more detailed account of work already published (A., 1922, i, 893).

Part Played by Iron and Fat in the Recovery of Rats from Chronic Experimental Anæmia. J. M. D. SCOTT (*Biochem. J.*, 1924, **18**, 347—350).—Rats were cured from subchronic anæmia by the administration of ferrous chloride when fed on diet of bread and whole milk. When the whole milk was replaced by skimmed milk and palm kernel oil the iron salt had no curative action. S. S. Z.

Method for Estimating the Retention of Calcium and Phosphorus in Young Growing Rats. M. A. BOAS (*Biochem. J.*, 1924, **18**, 425—432).—A method for estimating the retention of calcium and phosphorus in young growing rats for periods of 3 to 7 weeks is described. Rats on normal diet showed a retention which declined week by week, and smooth curves plotted from the figures obtained were similar in shape to the curve of normal growth. S. S. Z.

Mechanism of Vital Staining with Basic Dyes. M. McCutcheon and B. Lucke (*J. Gen. Physiol.*, 1924, **6**, 501—507).—The degree of staining obtained with basic dyes in living cells was compared in solutions containing ammonium hydroxide, sodium hydroxide, carbon dioxide, and hydrochloric acid. A greater degree of staining was obtained in a solution of sodium hydroxide than in one of ammonium hydroxide of the same p_H, which means that with constant extracellular reaction staining is hindered by intracellular alkalinity. With constant intracellular reaction, it is found that staining is favoured by increased extracellular alkalinity.
C. R. H.

Basic Peptones from the Mucous Membrane of the Stomach. K. Felix (*Z. physiol. Chem.*, 1924, **135**, 175—179).—The mucous membrane of the stomach of pigs gives on extraction with cold water peptones of a strongly basic character. These contain considerable quantities of the hexone bases, arginine, histidine, and lysine. They give the biuret reaction and generally the diazo-reaction and are very hygroscopic. E. M. C.

Animal Urease. O. Steppuhn and X. Utkin-Ljubovzov (*Biochem. Z.*, 1924, **146**, 115—121).—The livers of the dog and horse contain a small amount of urease, which is better detected in acid extracts than in the expressed juice from the organ. It is probably derived from vegetable sources. It is not mobilised during acidosis for the purpose of neutralising acidity, and it is concluded that it is devoid of physiological significance. J. P.

Autolysis. II. P. Rona and E. Mislowitzer (*Biochem. Z.*, 1924, **146**, 1—25).—The autolysis of guinea pig liver pulp at the optimum p_H 3·6 is inhibited by sodium chloride, bromide, sulphate, citrate, and tartrate in 0·2*M* concentration, whilst sodium acetate is inactive. At p_H 5—6·0, the action of these salts is reversed and autolysis is increased. The cations sodium, potassium, and calcium at p_H 3·6, in concentrations of from 1·0 to 0·5*N*, inhibit, and in concentrations between 0·25 and 0·1*N* increase autolysis. Within the former range of concentrations, sodium has a more marked inhibitory effect than potassium, whilst in the latter range potassium increases autolysis more than sodium. Calcium, in concentrations between 1·0 and 0·1*N*, has a greater increasing and a lesser inhibiting action than potassium. In 0·05*N* solution, the order of activity in increasing autolysis is $Na > K > Ca$. At p_H 5·0, a reversal of action, similar to that of the anions, is also observed in the case of the cations. Lithium and rubidium increase autolysis to a less extent than does sodium. J. P.

Autolysis. III. Autolysis of Phosphorus-poisoned Liver. P. Rona, E. Mislowitzer, and S. Seidenberg (*Biochem. Z.*, 1924, **146**, 26—35).—The autolysis of a phosphorus-poisoned guinea pig liver is greater than that of the normal liver. This is ascribed to the gradual increase in the hydrogen-ion concentration, since if the pulp be buffered at the optimum p_H 3·6 or at higher p_H, the extent of autolysis observed is normal. In the buffer-poisoned liver, the autolysis products have amino-nitrogen values from 70 to 100% higher than the normal. J. P.

Chemistry of Gaucher's Disease. E. EPSTEIN (*Biochem. Z.*, 1924, **145**, 398—414).—A histo-chemical and qualitative investigation of the "Gaucher substance" found in the cell vacuoles of the spleen from cases of Gaucher's disease. It is concluded that this substance is not homogeneous, and its formation is associated with a diminution in the nitrogen and an increase in the carbohydrate of the spleen. The ethereal extract of the affected spleen does not differ qualitatively or quantitatively from that of the normal organ, whilst the alcoholic extract, when precipitated with mercuric chloride, yields a colourless, micro-crystalline, phosphorus-free substance, m. p. 176°, capable of swelling in water, with the physical and chemical properties of a sphingogalactoside. The presence of such a substance is not demonstrable in the normal spleen. J. P.

Creatine and Creatinine in Muscle Extracts. F. S. HAMMETT (*J. Biol. Chem.*, 1924, **59**, 347—351).—Creatine is formed from creatinine in muscle tissue or its extracts on incubation or autolysis. The rate of this transformation is practically the same in extracts of brain- and muscle-tissues, when the two extracts are obtained from tissues from the same animals using Tyrode's solution as the extraction agent and phosphate mixture as buffer during simultaneous aseptic incubation at 37—38°. This rate is twice as great as that in buffered Tyrode's solution. It is further shown that in the brain, as in the muscle, there are no enzymes which produce creatine or which destroy creatinine or creatine. It is concluded that creatinine formation occurs in brain as well as in muscle, thus supporting Folin's view that creatinine formation is a function of the total normal tissue metabolism. D. R. N.

Succinic Acid in Muscle. I. D. M. MOYLE (*Biochem. J.*, 1924, **18**, 351—364).—Fresh ox muscle yields a small quantity of succinic acid. This yield is increased when the muscle of the ox, dog, sheep, rabbit, and possibly frog is incubated anaërobically in a phosphate buffer solution of p_H 7·0—8·4. A bigger yield of the acid is also obtained if glutamic or aspartic acid is added. The addition of sugar does not alter the yield, whilst the addition of certain pancreatic preparations markedly decreases it. In the red muscle of the rabbit a greater yield is obtained than in the white. A method for the determination of succinic acid is described. It is based on the volumetric determination of the silver in the silver succinate precipitate of the muscle extract after the removal of all other interfering constituents. S. S. Z.

Distribution and Variation of Carnosine in Cat Muscle. G. HUNTER (*Biochem. J.*, 1924, **18**, 408—411).—The carnosine content of various muscles in a number of cats has been ascertained. In the same animal, carnosine is a variable constituent of white muscle, but is approximately constant in red. S. S. Z.

Testing for Incipient Putrefaction [of Foodstuffs]. J. TILLMANS and R. OTTO (*Z. Unters. Nahr. Genussm.*, 1924, 47, 25—37).—The flesh of fish decomposes differently from that of mammals. Incipient decomposition of fish can be detected by determining the ammonia and amino-acid nitrogen, although this method fails to indicate the incipient decomposition of meat. Fish containing more than 0·03% of ammonia or more than 0·1% of amino-acid nitrogen, as determined by methods the details of which are given, may be considered to be in a state of incipient decomposition. Other methods of detecting incipient decomposition of fish, depending on the content of amino-acids and polypeptides, on oxygen absorption, and on the reduction of potassium nitrate and of methylene-blue, are described. The identification and determination of peptones, carbonic acid, indole, soluble nitrogen, and substances combining with iodine lead to uncertain or negative results and no new method of indicating the incipient decomposition of fish could be founded on these substances as criteria.

H. C. R.

Proteolytic Enzymes in the Thymus. G. WIDMARK (*Z. physiol. Chem.*, 1924, **135**, 122—128).—The soluble products of autolysis of acidified calf thymus contain enzymes showing optimum activity at p_H 5·6 and 7·6, respectively, comparable to those obtained by Hedin (A., 1923, i, 507) from milk, lymphatic glands, and kidney and by Zachrisson (*Upsala Läkaref förhandl.*, 1923, **28**, 333) from the liver. The insoluble products give a sodium chloride extract containing an enzyme with an optimum at about p_H 8·0.

E. M. C.

Reduction of Sodium Nitrate and Potassium Chlorate during the Putrefaction of Viscera. C. GHIGLIOTTO (*Ann. Falsif.*, 1924, **17**, 93—95).—Sodium nitrate and potassium chlorate are reduced rapidly during the putrefaction of animal organs.

W. P. S.

Reduction of Aromatic Nitro Groups by the Tissue of Guinea Pigs after Treatment with Proteins and during Anaphylactic Shock. IX. The Effect of Proteins. H. LÖHR (*Z. ges. exp. Med.*, 1923, **37**, 442—453; from *Chem. Zentr.*, 1924, i, 682).—The ability of isolated cells to reduce nitro groups, *e.g.*, in *m*-dinitrobenzene, can be increased by preliminary administration of milk and serum. The greatest activation was produced in the kidneys, followed by the muscles and the brain. The liver was practically unaffected. Peptone injection decreased reducing power. The same effect was also shown by peptone on muscle cells *in vitro* and also during anaphylactic shock. G. W. R.

Carotin. The Principal Cause of the Red and Yellow Colours in *Perillus bioculatus* (Fab.) and its Biological Origin from the Lymph of *Leptinotarsa decemlineata* (Say). L. S. PALMER and H. H. KNIGHT (*J. Biol. Chem.*, 1924, **59**, 443—449).—The yellow and red colours of the hypodermis of the stink-bug, *Perillus bioculatus* (Fab.), are due largely to carotin, which is derived from the food, chiefly the lymph of the potato-beetle, *Leptinotarsa decemlineata* (Say). The lymph of the potato-beetle is coloured exclusively by carotin, amounting to 0·0136% in the fresh lymph, which is about the same concentration as that found in fresh green leaves. Experiments showing that the amount of carotin deposited in the hypodermis of insects can be permanently modified by environment without removing the source of pigment require substantiation before they may be accepted as illustrating the inheritance of acquired characters. D. R. N.

Anthocyanin and Flavone-like Pigments as Cause of Red Colorations in the Hemipterous Families, *Aphididæ, Coreidæ, Lygæidæ, Miridæ,* and *Reduviidæ.* L. S. Palmer and H. H. Knight (*J. Biol. Chem.*, 1924, **59**, 451—455).—Red pigment in both phytophagous and predaceous families of Hemiptera is not limited to one type of substance, as water-soluble pigments appear to be more common than carotin. The aphid, *Tritogenaphis rudbeckia*, owes its vermilion colour chiefly to an anthocyanin-like pigment, although small quantities of carotin are also present. The red colour of the red and black patterned phytophagous box-elder plant-bug and other bugs is due to a flavone-like pigment. From these results it is difficult to understand how environment can cause a permanent modification of an insect colour pattern involving an animal pigment which is derived from the food and is subject to fundamental physiological processes of the protoplasm without first causing a permanent modification of the processes to which the derived pigment is subject. The view that the red pigment in insects can thus be modified and the modification become inheritable is weakened in the light of these findings that the pigment is likely to be a carotinoid, anthocyanin, or flavone derived from food. D. R. N.

Composition of Herring Roe. VI. Monoamino-acids of Ichthulin. K. Iguchi (*Z. physiol. Chem.*, 1924, **135**, 188—197; cf. Steudel and Takahashi, A., 1923, i, 729, 1257).—A fractionation of the monoamino-acids of ichthulin, the protein from herring eggs, has completed the data necessary for showing the fundamental identity of the protein in the ripe eggs and in the empty egg casing. E. M. C.

Gases of the Air-bladder of *Porichthys notatus.* C. W. Greene (*J. Biol. Chem.*, 1924, **59**, 615—621).—The oxygen content of the gas from the air-bladder of this fish ranges from 30% to 88·2%; the carbon dioxide from 0 to 2·4%; the nitrogen from 4·8% to 70%. The gas obtained after the bladder has refilled is not markedly different from the first sample. C. R. H.

Echinococcal Anaphylaxis. J. H. Botteri (*Z. ges. exp. Med.*, 1923, **37**, 175—183; from *Chem. Zentr.*, 1924, i, 682).—In echinococcal infections the hydatid fluid contains albuminoid and lipoid substances. The proteins, separated by salting out with sodium chloride and redissolved, give the anaphylactic reaction with the diseased animals. The reaction is still given after removal of coagulable proteins from the solution. Hydatid fluids, from oxen, giving no sulphosalicylic acid or biuret reaction and giving only a positive "ninhydrin" reaction, are found to be biologically active. The intensity of the reaction is correlated with protein content. Of the proteins isolated, euglobulins give the strongest reaction, followed by the pseudoglobulins. The albumins are scarcely reactive. Lipoids and products of protein hydrolysis do not produce anaphylaxis. The positive intracutaneous reaction given by hydatid fluid appears to be associated either with the presence of small amounts of protein which can be detected serologically but not chemically, or with the presence of differently constituted substances having anaphylactic properties.

G. W. R.

Acetaldehyde Content of the Urine in Normal and Pathological Conditions. W. Stepp and I. Rothman-Manheim (*Biochem. Z.*, 1924, **146**, 349—360).—In normal urines the amount of acetaldehyde excreted (2—4 mg. in 24 hours) is not influenced by withholding carbohydrates from the dietary nor by starvation, from which it is concluded that the formation and excretion of the aldehyde is not related to that of acetone. In cases of nephritis, nephrosis, uræmia, in liver affections, and in various other pathological conditions, no significant variations in acetaldehyde excretion were observed, whilst in cases of diabetes insipidus this was markedly increased (1·6—27 mg. per diem). Excretion of acetaldehyde is not of constant occurrence in diabetes, being most marked in, whilst showing no parallelism to, advanced glycosuria with associated ketonuria, but falling off in acidosis and in coma. As in normal cases, the excretion of acetaldehyde is not influenced by dietetic conditions. J. P.

Excretion of Amino-acids by Infants during Starvation and on a Protein-rich Diet. Formol Titration in Small Quantities of Urine. F. von Bemuth and F. Goebel (*Biochem. Z.*, 1924, **146**, 336—342).—In a newly-born child with a closure of the œsophagus and therefore unable to feed, abnormally high amino-nitrogen values were found in blood and urine. This is ascribed to an impairment of de-aminising powers induced by starvation. From feeding experiments in normal infants, the high amino-nitrogen excretion is ascribed to the high permeability of the kidney to amino-acids, a condition dependent to a certain extent on diet. Improvements in the Sörensen method of formol titration are described which render the process more readily applicable to small quantities of urine. J. P.

Are Guanidines Present in the Urines of Parathyroidectomised Dogs? I. Greenwald (*J. Biol. Chem.*, 1924, 59, 329—337).—The author's experiments did not afford conclusive evidence of an increased formation or decreased destruction of guanidines after parathyroidectomy, nor did they prove the absence of guanidines from the urines of parathyroidectomised dogs. There are only two well authenticated metabolic changes after parathyroidectomy, viz., lowered calcium content of serum or plasma, and diminished excretion of phosphorus in the urine. D. R. N.

Proteinogenous Amines. XVI. Excretion of Iminazoles in the Urine. K. K. Koessler and M. T. Hanke (*J. Biol. Chem.*, 1924, **59**, 803—834).—If urine be treated with lead acetate and sodium hydroxide, all the iminazole compounds are left in the filtrate. A series of determinations by the colorimetric method shows that the normal daily excretion of these compounds is between 120 and 220 mg. In cases of nephritis with nitrogen retention, the daily excretion is definitely lower than in the normal person on the same diet. C. R. H.

Urinary Hydrogen-ion Concentration in Normal Man during Fasting. ·Le Noir and A. M. de Fossey (*Compt. rend.*, 1924, **178**, 1632—1633).—During fasting, the value of p_H for human urine normally undergoes only very slight variation, but falls slightly if the subject indulges in prolonged muscular effort.

T. H. P.

Relation of the Alkaline-earth Metals to the Acidity of Urine. L. Lescœur and L. Moquet (*Compt. rend. Soc. Biol.*, 1923, **89**, 1036—1038; from *Chem. Zentr.*, 1924, i, 682).—Acidity in urine may be correlated with high specific gravity and high content of alkaline-earth and other salts. The elimination of magnesium in urine increases with the acidity. Calcium shows a less close relationship. G. W. R.

Colloids in the Urine and the Blood. J. Wohlgemuth and T. Koga (*Biochem. Z.*, 1924, **146**, 36—51).—The property of frothing shown by urine is ascribed to the presence of a positively charged colloid, since the property is lost by shaking the urine with kaolin but not with aluminium oxide. Starvation increases the amount of this colloid in the urine. If the urine be dialysed, the foam-forming colloid loses its positive charge and becomes amphoteric, a result which is ascribed to the removal of the cations which are responsible for the charge. The colloid is not affected by boiling or by low temperature (—12°), nor is its presence related to the surface tension of the urine. It contains nitrogen, and its particles have a size of 1 μ. Nephritic and icteric urines contain more of the colloid than normal urines. A similar foam-forming colloid is present in blood-sera, notably in nephritic sera, but it has a negative charge. Aqueous suspensions of blood-corpuscles foam but slightly on shaking, but on acidification with acetic acid this property is much increased. It is not influenced by kaolin or alumina. J. P.

Effect of Metallic Salts on the Bactericidal Action of Blood-plasma. L. E. Walbum (*Compt. rend. Soc. Biol.*, 1923, **89**, 1007—1010; from *Chem. Zentr.*, 1924, i, 681).—On addition of one drop of a 24-hour bouillon culture of *Bacillus coli* to fresh citrate plasma containing different metallic chlorides, the first effect with incubation at 37° was a diminution in bacterial numbers, followed eventually by an increase so that after 2 hours bacterial numbers were greater than originally. Considering the effect in the first period, it was found that with salts of calcium, magnesium, silver, ferric salts, and chromic salts the bactericidal effect increased with decreasing atomic weight. The reverse held for the platinum group, and for cobalt, nickel, and manganese. Intravenous injection of manganous chloride increased the bactericidal action of the blood in the case of a goat. G. W. R.

Poisoning from Barium Sulphate in an *X*-Ray Examination. E. DINSLAGE and F. BARTSCHAT (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 7—9).—A case of fatal barium poisoning due to the presence of barium carbonate in a sample of barium sulphate administered previous to an *X*-ray examination is described. H. C. R.

Action of Thorium-*X* on the Maturation of Eggs, the Germination of Seeds, and the Growth of Plants. AVERSENQ, DELAS, JALOUSTRE, and MAURIN (*Compt. rend.*, 1924, **178**, 1491—1492).—Experiments with eggs of *Ascaris lumbricoides* show that small doses of thorium-*X* increase the rate of maturation whilst larger doses much retard it. Similar effects are observed on the germination of seeds of *Raphanus*, and the growth of *Lemna polyrrhiza*. A. B. H.

Uranium Diuresis. R. HEILIG (*Z. ges. exp. Med.*, 1923, **37**, 163—174; from *Chem. Zentr.*, 1924, i, 684).—Subcutaneous injection of 3—15 mg. of uranium nitrate produced intense diuresis in dogs without, apart from a short period, increasing the output of sodium chloride. In the initial stages, loss of water from the blood took place accompanied by increase in hæmoglobin, erythrocytes, and residual nitrogen. In the later stages of diuresis, these effects disappeared. The effect of uranium nitrate appears to be principally on the kidneys, but extra-renal factors may also be involved. G. W. R.

Drug Resistance of Trypanosomes. C. VOEGTLIN, H. A. DYER, and D. W. MILLER (*J. Pharm. exp. Ther.*, 1924, **23**, 55—86).—A strain of trypanosomes resistant to arsenic may be produced by inoculating an animal which has previously been treated with an arsenical drug of a type which is slowly excreted; this resistance can be reduced by passing the strain through another host. Only arsenic in a compound of the type $R \cdot As\!:\!O$ is toxic to trypanosomes *in vitro*, and the toxicity of this type of arsenic compound is completely inhibited by the presence of a substance containing the sulphydryl group. It is suggested that the toxic action of the arsenic compound depends on a condensation of the latter with the glutathione of the organisms and a consequent derangement of their cell respiration. The variations in arsenic resistance of different strains are thus explained as being due to the different amounts of glutathione which may be present in the organisms in excess of their normal physiological requirements. C. R. H.

Comparative Studies on Narcosis with Chloroform and Dichloroethylene. Effect on Protein Balance of Rats. R. W. Rigler and R. Ringel (*Z. ges. exp. Med.*, 1923, **37**, 429—441; from *Chem. Zentr.*, 1924, i, 686).—Chloroform produces a marked decrease of respiration frequency, an effect which is not observed with *cis*-dichloroethylene. There is a pronounced rise in the curve for urine nitrogen where chloroform is administered. Both *cis*- and *trans*-dichloroethylene are without serious effect on the nitrogen balance. G. W. R.

Properties of the Constituents of Witte's Peptone. J. J. Abel and E. M. K. Geiling (*J. Pharm. exp. Ther.*, 1924, **23**, 1—27).—By half-saturation and subsequent complete saturation with ammonium sulphate of a solution of Witte's peptone, there were obtained two albumose fractions. From the filtrate a further fraction soluble in acid alcohol was obtained. The albumose fractions were only slightly toxic, but the alcohol-soluble fraction behaved physiologically like histamine. Further, this fraction gave the Pauly reaction. The authors consider that the toxic substance is histamine, but that its origin is not bacterial. C. R. H.

Active Principles of Peptone. A. J. Clark (*J. Pharm. exp. Ther.*, 1924, **23**, 45—54).—Peptones contain a substance, soluble in alcohol, having a physiological action resembling that of extracts of the posterior lobe of the pituitary; there is sometimes also found a second alcohol-soluble substance with sympathomimetic properties. No evidence could be found of the presence of histamine. The author considers that the lethal action of peptone injected intravenously is due to the alcohol-insoluble portion, although this portion is without action on isolated organs. C. R. H.

New Synthetic Nitrophenol Glucosides and the Disinfectant Action and Toxicity of the Nitrophenols. E. Glaser and W. Wulwek (*Biochem. Z.*, 1924, **145**, 514—534).—o-*Nitrophenol tetra-acetyl glucoside*, $C_6H_4O_2N\cdot O\cdot C_6H_7O_5(Ac)_4$, long, colourless needles, m. p. 158—159°, $[\alpha]_D^{18}$ +36·14°, is obtained by the action of an aqueous alkaline solution of nitrophenol on tetra-acetylbromoglucose in acetone, and on hydrolysis with ammonia in methyl alcohol it yields β-o-*nitrophenol glucoside*, $C_6H_4O_2N\cdot O\cdot C_6H_{11}O_5,H_2O$, colourless, hygroscopic crystals, m. p. 130—131°, having $[\alpha]_D^{14}$ —82·72°. m-*Nitrophenol tetra-acetyl glucoside*, m. p. 136—137°, $[\alpha]_D^{18}$ —18·26°, β-m-*nitrophenol glucoside* (+1H_2O), m. p. 167—168°, $[\alpha]_D^{22}$ —84·89°, p-*nitrophenol tetra-acetyl glucoside*, m. p. 174—175°, $[\alpha]_D^{18}$ —27·17°, and β-p-*nitrophenol glucoside* (+1H_2O), m. p. 164—165°, $[\alpha]_D^{23}$ —99°, are obtained in analogous manners. The three glucosides are hydrolysed by emulsin. The nitrophenols are intermediate in bactericidal power between phenol and the cresols, the meta compound being the most active, whilst the corresponding glucosides formed from them are devoid of disinfectant properties. The para compound is the most toxic of the three nitrophenols, whilst the derived glucosides have but a slight toxicity. This is correlated with the detoxication of phenols by conjugation with glucuronic acid in the animal organism. J. P.

Quantitative Protozoöcidal Comparison of some Opium Alkaloids. C. E. Bills and D. I. Macht (*J. Pharm. Exp. Ther.*, 1924, **23**, 261—268).—Adopting unity as representing the toxicity of morphine to *Paramœcium* at p_H 5·7, the degree of toxicity of various opium alkaloids is as follows: morphine 1, codeine 1, dionine 2, heroine 7, thebaine 30, pantopium (the total alkaloids of opium) 30, papaverine 30, peronine (benzylmorphine) 100. With increasing p_H (6·6—7·7), morphine becomes less toxic, whilst codeine, heroine, and thebaine become much more toxic. Some evidence exists in favour of the view that *Paramœcia* become more resistant to given opium alkaloids after being subjected to non-lethal doses of the same alkaloid. J. P.

Behaviour of Bacteria towards the Alkaloids. H. H. Green and I. Lonstein (*J. S. Afr. Chem. Inst.*, 1924, **7**, 6—8).—The authors have isolated a non-spore-forming aërobe from nicotine sheep-dips; the organism does not liquefy gelatin, does not form acid or gas from dextrose, lactose, sucrose, or glycerol, is non-chromogenic, and non-diastatic. It destroys nicotine rapidly when the latter is the sole source of food supply as regards nitrogen and carbon, but if grown in media containing ammonium salts or simple nitrogenous compounds the organism loses its power of destroying nicotine. The organism tolerates morphine and atropine in concentrations up to 2%, but its growth is inhibited by strychnine, brucine, and quinine. Numerous putrefying organisms will grow in media containing 0·2% of nicotine, morphine, or atropine but not in those containing strychnine, brucine, or quinine. W. P. S.

Diastases. The Two Enzyme Theory. K. Hizume (*Biochem. Z.*, 1924, **146**, 52—71).—The liquefying action of human salivary diastase is increased in the same way as the saccharifying power by potassium and sodium chlorides and bromides, whilst iodides and fluorides are devoid of action. Diluted blood-serum has a similar activating effect. Dialysis lowers the liquefying power of saliva on starch, and this is entirely regenerated by the addition of chlorides and bromides. Nitrates act in a similar way on dialysed and undialysed saliva, nitrites are less active, whilst sulphates have no action on undialysed, but regenerate the activity of dialysed saliva. Alkalis and acids exert the same influence on the liquefying properties as on the saccharifying action of salivary diastase. The liquefying and saccharifying powers of malt diastase are not affected by salts. Maltose and dextrose protect salivary diastase from inactivation by heat, whilst sucrose and lævulose are much less active in this respect. Chlorides, bromides, and diluted serum also protect the enzyme against heat-inactivation, whilst iodides and nitrates have no such action. Malt diastase is more easily inactivated by heat in the presence of chlorides and bromides than in their absence (cf. A., 1923, i, 1254). J. P.

Purification of Malt Diastase by Electro-dialysis and Electro-osmosis. II. R. Fricke (*Ber.*, 1924, **57**, [*B*], 765—768).—Improved methods are described for the preparation of the membranes and anode and for the regulation of the acidity of the solutions in the purification of malt diastase by electro-dialysis (cf. Fricke and Kaja, this vol., i, 469). The activity of the ultimate products is not thereby increased, but the heavy incidental losses of material are avoided. Increased attention to the acidity of the solutions in the electro-osmotic experiments has resulted in improved activity in the malt diastase, which, however, is very unstable in solution. H. W.

Influence of the New Sulphur-containing Amino-acid (Mueller) on the Activity of Pancreatic Amylase. M. L. Caldwell (*J. Biol. Chem.*, 1924, **59**, 661—665).—The new amino-acid (cf. A., 1923, i, 869; this vol., i, 438) exerts a favourable influence on the amylolytic action of pancreatic amylase which is similar to that previously observed with naturally occurring α-amino-acids. C. R. H.

Liver Amylase. O. Holmbergh (*Z. physiol. Chem.*, 1924, **134**, 68—96).—The value of $Sf=K\times$(g. maltose formed from starch)/(g. preparation used), K being the unimolecular reaction constant, differs for samples from various lobes of a pig's liver, the mean value being 0·0038. In all cases, it is very much less than the value obtained for a piece of pancreas. The addition of liver substance to a pancreas extract results in an activity lower than the sum of the activities of the two components. It appears that the liver contains a substance which inhibits pancreatic amylase. The activity of liver amylase is highest at p_H 6·9, and in presence of 0·008—0·5N-sodium chloride or potassium chloride, or 0·008—0·04N-calcium chloride. Sodium iodide decreases the production of maltose, but increases that of dextrose. Various methods of extracting liver amylase have been investigated. Dialysis at first increases the activity of the preparation, Sf increasing more than 500%, but further dialysis results in a decrease of activity. The action of liver amylase on starch is inhibited by maltose, but this inhibition disappears if the maltose is removed by maltase. If yeast is treated with toluene containing ethyl acetate so as to destroy the maltase, it no longer retains its power of increasing the activity of amylase. W. O. K.

Invertase. IV. H. von Euler and K. Josephson (*Ber.*, 1924, **57**, [*B*], 859—865; cf. A., 1923, i, 721; this vol., i, 466).—Elementary analyses of purified invertase (*If* 225—245) gave results which are closely similar to those of the proteins, the slight discrepancies being probably attributable to the presence of carbohydrates in invertase. Colorimetric determinations indicate the presence of tryptophan 5·5% and histidine <6%>2% in invertase; tyrosine is absent. As judged from the sulphur content, cystine is present to the extent of 2%. H. W.

Uniformity in Invertase Action. III. Stability of the Enzyme. J. M. Nelson and R. W. E. Kerr (*J. Biol. Chem.*, 1924, **59**, 495—527).—Invertase preparations could be made abnormal by treatment with dialysed iron, accompanied by an increase in the activity per unit of dry weight. Abnormal invertase prepared in this way is unstable at p_H about 4·5 and 25°. It can be re-stabilised by the addition of inactivated normal invertase preparation. This re-stabilisation may be effected in varying degree according to the concentration of the added inactivated normal invertase preparation, and is reversible with dilution. Normal invertase preparation which is rendered unstable by dilution is re-stabilised by the addition of gelatin, egg-albumin, or inactivated normal invertase preparation. At p_H 2·2 and 25°, abnormal invertase is less stable than normal invertase, and the addition of inactivated normal invertase preparation causes an increase in the stability of the former and a decrease in that of the latter. The rate of inactivation of invertase solutions at p_H 2·2 and 25° is higher in the more concentrated solutions and falls off in the latter part of the inactivation. The inactivation of concentrated invertase solutions brought about in this manner is partly reversible with dilution and changing the p_H from 2·2 to about 4·5, although the reversibility is not observed with less concentrated solutions. At p_H 4·8 and 60—65°, both the normal and the abnormal invertase preparations possess the same stability. D. R. N.

Characteristics of Invertase Action. J. M. Nelson and G. Bloomfield (*J. Amer. Chem. Soc.*, 1924, **46**, 1025—1043).—Arising out of the observation that different invertase preparations at different temperatures gave a maximum velocity of inversion at nearly the same sucrose concentrations (Nelson and Vosburgh, A., 1917, ii, 252), the influence of the temperature and of the hydrogen-ion concentration on the relation between the sucrose concentration and the rate of hydrolysis has been studied. The sucrose concentration at which the hydrolysis reaches its maximum velocity is independent of the temperature and hydrogen-ion concentration. Further, the limits of hydrogen-ion concentration within which the hydrolysis with invertase follows a normal course extend from p_H 2·75—3·3 (depending on the temperature) in the acid region to p_H 8·4 in the more alkaline region. Between 25° and 35°, the hydrogen-ion concentration at which invertase first shows inactivation decreases regularly. The zone of the optimum action of invertase at 25°, 30°, 35° lies between the hydrogen-ion concentrations p_H 4·5 and 5·0, which are narrower limits than previously determined. The relation between the activity (n) and the hydrogen-ion concentration approximately satisfies the equation for the dissociation residue curve, $\rho=[H^{\cdot}]/([H^{\cdot}]+k)$, where ρ is the fraction of the compound not dissociated and k is the dissociation constant, as claimed by Michaelis and Davidsohn (A., 1911, i, 1052). The temperature does not affect [illegible]. The temperature coefficient of the hydrolysis of [illegible] presence of invertase increases with decreasing acidity, hence the hydrolysis is inherently different from that by acid, where the same coefficient is independent of the hydrogen-ion concentration. The hydrolysis of sucrose is thus shown to involve two distinct stages, one of which is characterised by the sucrose concentration at which the hydrolysis reaches its maximum velocity and is independent of the temperature and acidity, whilst in the other it changes with each of these. A. C.

Calculation of the Activity-p_H Curve of Invertase. H. von Euler, K. Josephson, and K. Myrbäck (*Z. physiol. Chem.*, 1924, **134**, 39—49).—Assuming that the adsorption compound between invertase and sucrose dissociates as a weak acid between p_H 5 and p_H 8 and that the undissociated compound only is active, the variation of the rate of inversion with the p_H can be calculated. The experimental results agree well with theory. If, as has been shown to be probable by Willstätter and Kuhn (cf. A., 1923, i, 401), raffinase is identical with invertase, and this enzyme has an affinity constant for raffinose of only about 1/15 of that for investase, then it may be shown by calculation that the variation with p_H of the rates of fermentation of the two sugars should be very similar, as is found experimentally. W. O. K.

Affinity of Invertase for Different Sugars. II. K. Josephson (*Z. physiol. Chem.*, 1924, **134**, 50—67).—Invertase suffers no loss of activity when it is kept for 30 minutes at p_H 2·63. There is thus no destruction of invertase due to acid alone. The depressing effect of acid on the activity of invertase which appears when the inversion is carried out in a medium more acid than p_H 4·5 (the optimum p_H) is shown to be largely accounted for by the change in the affinity constant K_M of the enzyme for the substrate occasioned by the low p_H. A small discrepancy between the theoretical and experimental results is probably caused by the basic dissociation of the enzyme-substrate compound. Inversion is inhibited by dextrose and lævulose less at p_H 2·75 than at p_H 4·5. In the case of dextrose, the inhibition is maximum at p_H 4·5, whilst in the case of lævulose, inhibition continues to increase with the p_H. W. O. K.

Hydrolysis of the Endosperm of *Phytelephas macrocarpa* by its own Enzymes. F. J. Paton, D. R. Nanji, and A. R. Ling (*Biochem. J.*, 1924, **18**, 451—454).—Vegetable ivory shavings contain an enzyme which hydrolyses the mannan present in them to mannose and a trisaccharide which is presumably mannotriose. The hydrolysis was greatest at about p_H 4·2. When the enzyme is allowed to act for a long period, namely, 10 days, mannose alone is produced. It is probable, therefore, that the trisaccharide is an intermediate product. S. S. Z.

Synthesising Action of α-*d*-Mannosidase in Presence of Ordinary Glycol and Glycerol. H. Hérissey and J. Cheymol (*Compt. rend.*, 1924, **178**, 1372—1374).—Combination of mannose with glycol or glycerol is effected by the action of the α-*d*-mannosidase contained in germinated lucerne seeds (cf. this vol., i, 234). T. H. P.

Enzymic Hydrolysis of Hexose-monophosphoric Acid by Extracts of the Femur. Y. TAKAHASHI (*Biochem. Z.*, 1924, **146**, 161—163).—The hexose-monophosphate prepared by Neuberg (A., 1918, i, 423) by partial hydrolysis of hexose-diphosphate, is hydrolysed by aqueous extracts of the femur with the liberation of phosphoric acid (cf. Robison, A., 1922, i, 730). J. P.

Dried Yeast. H. SOBOTKA (*Z. physiol. Chem.*, 1924, **134**, 1—21).—The rate of fermentation of dextrose by yeast dried by various methods has been measured by determining the rate of production of carbon dioxide. With such dried yeasts there usually occurs a more or less marked period of induction. Increase of the concentration of the yeast decreases this period. If the yeast is first of all incubated with sugar solution the incubation period disappears. After being ground up in a mortar, dried yeast ferments sugar more slowly. Determination of the sugar at intervals during the fermentation by dried yeast shows that a certain disappearance of the carbohydrate takes place, amounting to from 20—50% of the sugar used, which cannot be accounted for by the carbon dioxide produced. W. O. K.

Mechanism of Alcoholic Fermentation. III. A. LEBEDEV (*Z. physiol. Chem.*, 1924, **134**, 160; cf. this vol., i, 464).—The liquid obtained after fermentation of sugar in presence of phosphate, on treatment with lead acetate and hydrogen sulphide, yielded no osazone but a white precipitate of either hydrazone or hydrazide. W. O. K.

Adenine Hexoside from Yeast. P. A. LEVENE (*J. Biol. Chem.*, 1924, **59**, 465—472).—The sugar constituent in adenine hexoside from yeast (A., 1912, i, 320) appears to possess certain peculiarities and differs from other known hexoses. It is not oxidised by bromine water and hence is ketonic, although apparently it is not a common β-ketohexose (A., 1915, ii, 494). The mutarotation of the phenylosazone of the new sugar closely resembles that of *d*-gulosazone, the initial rotation being practically 0° and the equilibrium slightly to the right. The m. p. of the new osazone is 165° (corr.), which is nearly the same as that of gulosazone, although the decomposition points are 208° and 180°, respectively. It further differs from gulosazone in being less soluble in alcohol and in water. These differences are more marked in the two *p*-bromophenylosazones. Taking dextrose as a standard of reduction, 1 g. of the hexoside should yield 0·6 g. of the sugar, whereas the maximum yield obtained from the hexoside was only 0·18 g. Further, on the basis of the rotation of the osazones, the sugar should belong to *d*-series, but *d*-sorbose rotates to the left, whereas the new sugar is dextrorotatory. Thus the new sugar does not seem to be identical with any one of the known β-ketohexoses. D. R. N.

Effect of Nitrogenous Nutrition on the Activity of Brewer's [illegible] [illegible] BAX (*Compt. rend. Soc. Biol.*, 1923, **89**, 1044—1045; [illegible] *Zentr.*, 1924, i, 680).—Fermentation with brewer's yeast is most active and produces the maximum amount of ethyl alcohol and acid at 15° in a bouillon containing 0·1% of ammonium hydrogen carbonate. G. W. R.

Variability of Lactic Acid Fermentation. A. LUMIÈRE (*Ann. Inst. Pasteur*, 1924, **38**, 344—357; cf. this vol., i, 353).—The author replies to criticisms of his previous work on the subject, and brings forward further experimental evidence in support of his contention that, provided his technique is rigidly followed, lactic acid fermentation is a perfectly regular process, both in normal media and in the presence of small concentrations of antiseptics, and, in the latter case, regardless of whether or not the bacteria used are acclimatised to the antiseptic. C. R. H.

Fermentation of the Unsaturated Dicarboxylic Acids. I. Fumaric Acid. J. H. QUASTEL (*Biochem. J.*, 1924, **18**, 365—380). —Succinic and fumaric acids are fermented by *Bacillus pyocyaneus*, with the production of lower fatty acids. In the case of fumaric acid, acetic acid is chiefly formed. This fermentation is accelerated by aëration, and proceeds more rapidly in the case of fumaric acid than in that of succinic acid. A 1% solution of ammonium fumarate is entirely utilised in 30 hours. The fermented fumarate medium gives colour tests with nitroprusside and with guaiacol due to the formation of pyruvic acid. The colour tests can be utilised as a test for differentiating *B. pyocyaneus* and *B. fluorescens liq.* from other bacteria capable of growing on a fumarate medium and which do not give these colour reactions. From the quantities of oxygen utilised and carbon dioxide formed during the fermentation of a known amount of fumaric acid a scheme representing the intermediate stages of fermentation in which oxalacetic acid figures is advanced; 90% of fumaric acid can be accounted for in the fermentation. S. S. Z.

Optimum and Limiting Concentrations of Hydrogen Ions for Bacterial Cultures. Tendency of Cultures to Approach the Optimum Concentrations. CLUZET, ROCHAIX, and KOFMAN (*Compt. rend.*, 1924, **178**, 1638—1639).—Cultures of *Bacillus coli*, *B. paratyphosus* B, and of Ebert's and Flexner's bacilli exhibited optimum and lower and upper limiting concentrations of hydrogen ions, these being different for the different organisms. During normal bacterial growth, the cultures tended to become gradually more alkaline but not to overstep the optimum hydrogen-ion concentration. If development is restricted owing to excessive acidity or alkalinity, the bacteria appear to exert an alkaligenic or acidogenic function, the reaction becoming progressively displaced towards the optimum value. T. H. P.

Effect of Iron and Zinc on the Development of *Aspergillus niger* in the Presence of Dextrose. A. FROUIN (*Compt. rend. Soc. Biol.*, 1923, **89**, 986—988; from *Chem. Zentr.*, 1924, i, 679). —The favourable effect of zinc and ferrous iron on the growth of *Aspergillus* in the presence of sucrose cannot be attributed to the presence of dextrose. Ferrous iron is unfavourable to the formation of dry mycelial tissue, but favourable to spore formation. G. W. R.

Transformation of Quinic Acid by Moulds. W. Butkewitsch (*Biochem. Z.*, 1924, **145**, 442—460).—The coloration observed to develop in cultures of *Citromyces* and *Penicillium* containing sodium quinate (A., 1922, i, 707) is ascribed to the formation of condensation products (with iron) by phenolic compounds into which quinic acid is transformed by the moulds. Protocatechuic acid is the most important of these phenols, but pyrocatechol, quinol, and quinone are supposed also to be formed. The subsequent disappearance of the coloration in old cultures is ascribed to the decomposition of the condensation products with formation of oxalic acid, which is later oxidised to carbon dioxide. Only those moulds which can bring about the formation of the intermediate phenolic compounds from quinic acid are able to utilise it as a source of carbon, and both processes are influenced in the same way when zinc sulphate is added to the culture. Moulds capable of forming phenolic compounds from quinic acid also ferment sugar with formation of citric acid, and a possible correlation of the two processes is suggested. These results are regarded as opposing the view of Kostytschev (A., 1921, i, 83) that quinic acid is first transformed by moulds into sugar.
J. P.

Comparison of Yields from the Point of View of Energy in the Development of Moulds utilising Carbohydrates or Proteins, and Specific Dynamic Action. E. F. Terroine, R. Bonnet, R. Jacquot, and G. Vincent (*Compt. rend.*, 1924, **178**, 869—872).—*Aspergillus niger* and *A. oryzæ* were cultivated in solutions of glucose to which ammonium sulphate had been added, of silk peptone, and of gelatin, the growths being analysed from the thermal point of view. The results, together with those obtained in the course of other investigations (Terroine, Bonnet, and Joessel, *Compt. rend.*, 1923, **177**, 900), lead to the generalisation that in living organisms formation of one carbohydrate from another involves extremely small energy loss, which is increased when carbohydrate is formed from fat and considerably so if from proteins. The energy utilisation coefficients of carbohydrates and proteins are in the ratio of about 100 to 140. H. J. E.

Metabolism of Acid-fast Bacteria. I. H. Braun, A. Stamatelakis, and S. Kondo (*Biochem. Z.*, 1924, **145**, 381—397).—An investigation of the growth of the acid-fast Timothy bacillus, various strains of butyric bacillus, urine and Trumpet bacilli in nutrient media containing various sources of carbon (organic acids, alcohols, and carbohydrates), nitrogen (amino-acids, urea, and uric acid), and inorganic salts. J. P.

Susceptibility of Lipases of Various Origin to Toxins. P. Rona and H. Petow (*Biochem. Z.*, 1924, **146**, 144—152).—The susceptibility to toxic inactivation (A., 1923, i, 1258) shown by [illegible] pancreatic, liver, and serum lipases is of the same order as that of the crude aqueous extracts containing these enzymes. The specific reactions of the lipases to quinine and atoxyl are preserved in artificial mixtures of the enzymes, serum lipase being inactivated by quinine, and serum and liver lipases by atoxyl. J. P.

Kinetics of Trypsin Digestion. II. Conditions Under Which the Reaction is Unimolecular. J. H. NORTHROP (*J. Gen. Physiol.*, 1924, **6**, 417—428).—If certain conditions are observed, the hydrolysis of casein by trypsin is accurately represented by the unimolecular formula $dx/dt=KE(A-x)$, where K is a constant, E is the quantity of enzyme used, A is the original concentration of casein, and x the concentration of casein at the time t. The conditions are that the temperature is low, to prevent inactivation of the trypsin, that much trypsin is used so that inhibition by the products of the reaction is negligible, and that the course of the reaction is followed by determining the actual amount of casein present at various times so that the effect of consecutive reactions is eliminated. Under these conditions also, the effect of variations in the initial concentration of the trypsin is predicted by the formula, but with increasing casein concentrations the value of K decreases and ultimately becomes nearly inversely proportional to the casein concentration. It is suggested that this is due to the existence of an equilibrium between casein and water in which casein can be replaced by the first cleavage products, since, if casein is dissolved in a freshly-prepared solution of digested casein, the reaction is typically unimolecular in every respect. W. O. K.

Kinetics of Trypsin Digestion. III. The Course of the Reaction with Constant Substrate under Conditions causing Inactivation of the Enzyme. J. H. NORTHROP (*J. Gen. Physiol.*, 1924, **6**, 429—437).—When gelatin is hydrolysed in concentrated solution by a large amount of trypsin at 60° and at p_H 6·0, inactivation of the trypsin takes place, and so the reaction is apparently not unimolecular. If, however, determination is made by the method of Northrop and Hussey (A., 1923, ii, 271) of the trypsin present at various times during the course of the reaction, it appears, from theory and experiment, under these conditions, (*a*) that the rate of reaction is proportional to the concentration of trypsin present at the time, (*b*) that the reaction is approximately unimolecular if the total hydrolysis observed is taken as the amount of substrate available, (*c*) that the velocity constant calculated in this way should agree with the constant for the decomposition of the enzyme, and that it should be independent of the concentration of the enzyme instead of proportional to it, and (*d*) that the total amount of substrate decomposed should be proportional to the amount of trypsin added at the beginning instead of independent of it. W. O. K.

Kinetics of Trypsin Digestion. IV. The Course of the Reaction when both Substrate and Enzyme Concentrations are Decreasing. J. H. NORTHROP (*J. Gen. Physiol.*, 1924, **6**, 439—452).—When edestin is hydrolysed by trypsin at p_H 7·0 at

40° in the presence of a high concentration of sodium chloride which decreases the activity of the trypsin and increases the solubility of the edestin, rapid inactivation of the trypsin occurs, and the reaction follows the equation $K=[\log(A_1/A_2)]/(T_1-T_2)E_t$, where A_1 and A_2 are the concentrations of the edestin at times T_1 and T_2 respectively and E_t is the concentration of the enzyme during the interval T_1-T_2. If it is assumed that the activity of the enzyme decreases unimolecularly, the theoretical results are obtained when high enzyme and low edestin concentrations are used. With low enzyme and high edestin concentrations, the effects of the products on the reaction become too large to be negligible. W. O. K.

Action of Chymosin on the Proteins of Milk. I. Action of Chymosin on Colostrum. J. ZAYKOWSKY (*Biochem. Z.*, 1924, **146**, 189—197).—From a comparison of the coagulating action of chymosin (rennin) on colostrum and on milk at varying acid concentrations, support is gained for the view that rennin and pepsin are not identical. J. P.

Detection of Ferment Processes Conditioned by Immunisation. I. E. KUPELWIESER (*Biochem. Z.*, 1924, **145**, 492—504).—Using the refractometric method described by Pregl and de Crinis (*Fermentforschung*, 1917, **2**, 58) and in contrast to the findings of these authors, no proteolytic action of serum on placenta proteins could be demonstrated in cases of pregnancy. J. P.

Detection of Ferment Processes Conditioned by Immunisation. II. E. KUPELWIESER and H. WASTL (*Biochem. Z.*, 1924, **145**, 505—513).—The sera of guinea pigs immunised with inactivated ox-serum have no proteolytic action on the antigen (cf. Pfeiffer and Mita, *Z. Immunitätsforsch.*, 1910, **6**, 18; Abderhalden and Pinkussohn, *Z. physiol. Chem.*, 1910, **64**, 100). J. P.

Proteinogenous Amines. XVII. Faculty of Normal Intestinal Bacteria to form Toxic Amines. XVIII. Production of Histamine, Tyramine, and Phenol in Laboratory Media by Intestinal Organisms. XIX. Factors involved in the Production of Phenol by the Colon Group. XX. Presence of Histamine in the Mammalian Organism. M. T. HANKE and K. K. KOESSLER (*J. Biol. Chem.*, 1924, **59**, 835—853, 855—866, 867—877, 879—888. **XXI. Intestinal Absorption and Detoxication of Histamine in the Mammalian Organism.** K. K. KOESSLER and M. T. HANKE (*ibid.*, 1924, **59**, 889—903).—XVII.—The action was observed of the mixture of bacteria in human fæces on histidine and tyrosine in a synthetic medium composed of salts and glycerol. Out of a series of twenty-six cases, it was found that 62% decarboxylated histidine, 65% decarboxylated tyrosine, and 46% could do both. Phenol was [illegible] produced from tyrosine; in three cases small amounts of [illegible] lactic acid were obtained. During the bacterial action the hydrogen-ion concentration of the fluid uniforml increased.

XVIII.—The decarboxylating action on histidine and tyrosine o two strains of colon bacilli was studied in milk, blood broth, an ascitic fluid broth. Amines were only produced in media containin carbohydrate and in which an acid reaction was developed. Th organism which produced tyramine in an acid medium produced phenol in an alkaline one.

XIX.—An extension of the preceding paper emphasising th authors' view that amine production is a protective mechanism o the bacteria against a rise in hydrogen-ion concentration of th medium.

XX.—Details are given of a method for the colorimetric determination of histamine in mixtures such as intestinal contents. In human fæces, there were found 6—20 mg. of histamine in 500 g. of material, and amounts of the same order of magnitude in cæcal contents. No evidence was found of the presence of histamine in the human liver, but it was demonstrated in the liver of the dog.

XXI.—A physiological study was made of the systemic effects observed after the introduction of histamine into different parts of the alimentary canal. A comparison of the rate of absorption, as measured by the disappearance of the substance from the alimentary canal, with the mildness of the resulting systemic effects, leads the authors to conclude that histamine may be detoxicated during its passage through the intestinal wall. C. R. H.

Culture of Moulds on Amino-acids and Mechanism of the Specific Dynamic Action. E. F. Terroine, S. Trautmann, R. Bonnet, and R. Jacquot (*Compt. rend.*, 1924, **178**, 1488—1490). —By growing *Aspergillus niger* and *A. oryzæ* on media containing glycocoll, alanine, valine, leucine, or glucosamine, it is shown that the energy liberated is constant and independent of the nature of the amino compound or organism. The energy change must therefore be associated solely with de-aminisation. A. B. H.

Production of Carbamide during Ammonification by the *Microsiphoneæ*. G. Guittonneau (*Compt. rend.*, 1924, **178**, 1383—1385).—When grown in an inorganic solution to which peptone was added as sole organic nutriment, certain of the *Microsiphoneæ* produced carbamide in considerable proportions and at the same time ammonium salts neutral to phenolphthalein accumulated in the liquid. The carbamide may be formed as a waste product or may be an intermediate compound in the assimilation of the hydrolytic products of the peptides. As regards its practical significance, carbamide readily enters the general cycle of vegetation owing to its transformation in the soil into ammonium carbonate, and, moreover, most plants secrete urease.

On the other hand, such liberation of carbamide results in loss of gaseous nitrogen if it is produced in contact with the nitrous acid displaced from nitrites by the acid formed in the various fermentations of carbonaceous material. These phenomena may occur in the soil and also help to explain the enormous losses of nitrogen taking place during the purification of sewage. T. H. P.

Occurrence of Peroxide in Cultures of *Pneumococcus*. O. T. Avery and H. J. Morgan (*J. Exp. Med.*, 1924, **39**, 275—287).—Peroxide formation was observed with various strains of *Pneumococcus, Staphylococcus hæmolyticus*, and *S. mucosus*, but not with *S. aureus*. With the first-named, there must be free access of air, and absence of catalase, peroxydase, etc.; the product is unstable, and conditions leading to its disappearance are mentioned.

Chemical Abstracts.

Participation of a Peroxydase in the Appearance of Pigment in *Drosophila melanogaster* (Lœw.). de Luna (*Compt. rend.*, 1924, **178**, 878—881; cf. this vol., i, 348).—Both an oxydase and a peroxydase play a part in the pigmentation of *Drosophila*; the former is probably tyrosinase, and the distribution of these enzymes is similar to that of the pigment. Rate of pigmentation is a function of temperature, but anæsthetics retard the fixation of oxygen on the colourless matter (A., 1904, ii, 831).

H. J. E.

Influence of *X*-Rays on the Catalase of Liver. A. Maubert, L. Jaloustre, P. Lemay, and C. Guilbert (*Compt. rend.*, 1924, **178**, 889—891; cf. Maubert, Jaloustre, and Lemay, A., 1923, i, 723).—The effect of *X*-rays is to decrease the activity of liver catalase in proportion to the duration of exposure and the intensity of radiation. Detailed results are given, but comparison is difficult as the catalase preparations used were not identical in each case.

H. J. E.

Sorptive Power of Metallic Hydroxides [for Invertase]. II. H. von Euler and R. Nilsson (*Z. physiol. Chem.*, 1924, **134**, 22—38).—Freshly precipitated lanthanum hydroxide adsorbs invertase even more completely than does aluminium hydroxide. It adsorbs more at p_H 8·1 than at p_H 5·6. Its power of adsorption decreases on keeping. The invertase adsorbed by lanthanun hydroxide is not adsorbed irreversibly unless the hydroxide is precipitated in presence of the enzyme, when some inactivation takes place. W. O. K.

Coagulation and Vegetable Life. J. Amar (*Compt. rend.*, 1924, **178**, 1317—1319; cf. this vol., i, 687; ii, 144).—Experiments on starch, on beans, and on the leaves of the spindle tree are described, the results indicating the marked de-coagulating effects produced by sodium chloride and other sodium salts and hence the importance of such salts in promoting osmotic interchanges and the general health of the vegetable organism. T. H. P.

[illegible] of Ozone by Green Plants. H. Coupin (*Compt.* [illegible] 178, 1572—1573).—Some evidence has been obtained that small quantities of ozone are given off, together with oxygen, from green plants when placed in a damp chamber in the light for 24 or 48 hours. Since in the dark, or with plants devoid of chlorophyll, no ozone is produced, it is concluded that ozone production is probably connected with carbon dioxide assimilation. J. W. B.

Equilibrium of the Cellular Constituents and Intensity of the Oxidations of the Cell. Imbibition and Oxidation. Case of Reviviscent Plants. A. Mayer and L. Plantefol (*Compt. rend.*, 1924, **178**, 1385—1388).—The authors have investigated the proportions of carbon dioxide formed when *Hypnum triquetrum*, soaked in water to bring it to a reproducible degree of imbibition and then allowed to dry to different extents, is kept in an enclosed space in the dark at 20°. The respiratory intensity either passes through a maximum at 50—60% of water in the moss, or gradually increases to a constant, or passes through a maximum at about 40% of water, according as it is referred to 1 g. of the wet moss, or to 1 g. of the dry matter, or to 1 g. of the water present. It is concluded that, other things being equal, there are definite proportions of water and of the other constituents of the cell for which the cellular oxidations exhibit a maximum intensity. T. H. P.

"Auximones," and the Growth of the Green Plant. N. A. Clark and E. M. Roller (*Soil Sci.*, 1924, **17**, 193—198).—*Lemna major* was grown in a series of artificial culture solutions and compared with that grown in soil suspensions. Healthy growth and reproduction depended on a requisite proportionality of dissolved salts. Neither "auximones" (Bottomley) nor organic matter were essential. In the absence of these latter, during 4 months closely followed the equation: $\log_{10}N/N_0=k(t-t_0)$, where N=number of plants present and t=time. A. G. P.

Effect of General Anæsthetics on the Respiration of Cereals. I. Carbon Dioxide Production. E. P. Smith (*Ann. Bot.*, 1924, **38**, 261—272).—Chloroform, ether, and ethyl alcohol in varied concentrations have similar effects on the carbon dioxide output from seedlings of wheat, rice, and oats; the first effect is a decrease in the rate of respiration, followed by an increase to a maximum and a final depression. With chloroform, recovery is possible only after very short exposures, whether continuous or intermittent; with ether recovery can take place even after 6 hours' exposure, provided the respiration does not fall below 60%. Experiments with the corolla of *Ipomœa* indicate that the effect of the anæsthetic on the permeability to carbon dioxide of the plasma membrane must also be taken into account, and that the apparent maximum respiration after treatment with an anæsthetic may be due to a release of carbon dioxide retained during a period of decreased permeability. E. M. C.

Anaërobic Experiments with Argon. W. A. Cannon and E. E. Free (*Carnegie Inst. Yearbook*, 1921, **20**, 63).—Experiments with roots and other parts of plants under partial anaërobic conditions show that the amount of oxygen necessary for growth the same when nitrogen or argon is used as the diluent gas, but less in the case of helium and hydrogen. The difference is probably concerned with the relative rates of diffusion of oxygen through the gases. A. A. E.

Carbohydrate–Amino-acid Relation in the Respiration of Leaves. H. A. Spoehr and J. M. McGee (*Carnegie Inst. Yearbook*, 1921, **20**, 60—61).—Carbon dioxide evolved in respiration was determined by a conductivity method. The stimulating effect of amino-acids (glycine, alanine, and asparagine) is most marked with dextrose as the carbohydrate food, noticeable with sucrose but not with mannose, and depressed by lævulose. No explanation is advanced. A. A. E.

The First Carbohydrates that Originate during the Assimilatory Process. Physiological Study with Variegated Leaves. T. Weevers (*Proc. K. Akad. Wetensch.*, 1924, **27**, 46—56).—In ten out of twelve different plants examined, the variegated parts of the leaves contain only sucrose, and the green parts both sucrose and monoses. The presence of monoses in the assimilating leaf-parts and their absence from the non-assimilating full-grown variegated leaves support the view that, in these plants, starch arises from the monoses and that the latter are, in general, the first sugars to be synthesised during the process of carbon assimilation. Confirmation of this view is furnished by the absence of starch as reserve material from three of the species, namely, *Aspidistra*, *Chlorophytum*, and *Ophiopogon*, which contain starch only in the stomata of both the variegated and the green parts of the leaf.

Complete proof has been obtained by depleting the full-grown leaves of the variegated *Pelargonium* of their sugar and starch by keeping the plants in the dark for two or three days and then exposing them to sunlight. Under these conditions, the first sugars to be formed as assimilation takes place are monoses, sucrose and starch appearing only later. Conclusive evidence is not available concerning the character of the initial monose, but in *Pelargonium zonale* lævulose seems to preponderate.

The variegated parts of the plants which contain sucrose contain also invertase, the fact that inversion does not occur in the living tissues being probably due to difference in localisation of the sugar and enzyme in the cell. T. H. P.

Nitrogenous Metabolism of the Higher Plants. V. Diurnal Variations in the Protein Nitrogen of Runner Bean Leaves. A. C. Chibnall (*Biochem. J.*, 1924, **18**, 387—394).—There is a definite fall in the protein content of bean leaves at night, due to the breaking down of the cytoplasmic material. The nitrogenous products of this protein decomposition are translocated away from the leaf. S. S. Z.

[illegible] Metabolism of the Higher Plants. VI. Rôle [illegible] the Metabolism of the Mature Plant. A. C. [illegible] 1924, **18**, 395—404).—The decomposition products arising from protein metabolism in bean leaves consist in large part of asparagine and other unknown substances containing free amino-nitrogen. Asparagine seems to be the chief agent whereby nitrogen in a form suitable for re-synthesis of protein is conveyed from one part of the plant to another. S. S. Z.

Nitrogenous Metabolism of the Higher Plants. VII. Leaf Protein Metabolism in Normal and Abnormal Runner Bean Plants. A. C. CHIBNALL (*Biochem. J.*, 1924, **18**, 405—407).—The protein degradation products of two normal and two abnormal plants are given. S. S. Z.

Carbon Dioxide Production of Plant Roots as a Factor in the Feeding Power of Plants. F. W. PARKER (*Soil Sci.*, 1924, **17**, 229—247).—The carbon dioxide evolution of various plant roots differed considerably, but no relationship between this factor and the feeding power of the plant (as determined by plant composition) was found. The removal of carbon dioxide from media by aspiration had no effect on the composition of the plants. The amount of the various nutrient elements absorbed by plants per gram of carbon dioxide excreted by the roots differed with the plant type. A. G. P.

Variation of the Iodine in *Laminaria flexicaulis* at the Period of the Annual Shooting. P. FREUNDLER (*Compt. rend.*, 1924, **178**, 1625—1628; cf. this vol., i, 354).—The results of further analyses show that the variations in the iodine content of this alga are influenced by the principal factors which intervene in enzymic reactions. Such variations constitute one of the manifestations of the disturbance of the equilibria between the alga and the sea, and between the alga and the air, and appear to be due to temporary, progressive, and reversible modification in the state of combination of the iodine. T. H. P.

Extraction of Pectin from the Fruit Rind of the Lime (*Citrus medica acida*). F. HARDY (*Biochem. J.*, 1924, **18**, 283—290).—Under similar time conditions, the total quantity of pectinogen obtained by extraction from the dried white rind of lime fruits varies directly with the hydrogen-ion concentration of the extracting medium when carried out at temperatures below boiling point. The quantity also varies directly with the temperature if the final reaction of the extract is less acid than p_H 2·0. Alkaline extracts do not contain pectinogen. Autoclave treatment in acid medium hydrolyses the pectinogen. The viscosity of the extracts depends more on the conditions of extraction than on the pectinogen content. S. S. Z.

Pectins of *Apium graveolens*, of the Tubers of *Stachys tuberifera*, and of the Rind of *Citrus vulgaris*. Biochemical Method of Characterising Galactose applied to the Study of the Composition of these Pectins. J. CHARPENTIER (*Bull. Soc. Chim. biol.*, 1924, **6**, 142—156).—In the alcoholic extract of the roots of *Apium graveolens* the presence of sucrose, mannitol, and a small quantity of a reducing sugar was demonstrated. The pectin of the same plant was obtained as a white powder, $[\alpha]_D$ +154·5°, which was coagulated in aqueous solution by the pectase of lucerne, by lead acetate, calcium and barium hydroxides, and by traces of hydrochloric acid. It yielded mucic acid when treated with nitric acid, and *d*-arabinose on hydrolysis with dilute sulphuric acid. The pectins of *Stachys tuberifera* and of *Citrus vulgaris*, with $[\alpha]_D$ +119·8° and +170·5°, respectively, also yielded mucic acid and arabinose and possessed properties similar to those of the pectin of *Apium*. From the hydrolysis product of the pectins of *Apium* and *Citrus*, treated with 70% aqueous ethyl alcohol in the presence of emulsin for 3 months, crystalline β-ethyl galactoside (m. p. 158—159°; $[\alpha]_D$ −5·3°) was isolated, yielding on hydrolysis dextrorotatory galactose and on oxidation mucic acid. It is concluded that the latter does not arise from galacturonic acid, and the presence of a galactan in these pectins is established. J. P.

Chemical Nature of the Cellulose Membrane. F. M. Wood (*Ann. Bot.*, 1924, **38**, 273—298).—The author has reinvestigated the methods of preparation and staining of plant-tissues in order to differentiate between cellulose and pectic compounds. The best conditions of preparation for double staining are those giving minimum oxidation and maximum hydration without disintegration. Tests for oxycellulose were made on a large number of stem and root sections both in the fresh state and after the use of many fixatives. Alcohol and glycerin should be avoided on account of their obstinate retention by cellulose and their liability to wash into the pectin and so disturb its reactions to dyes. Pectin is stained by hydrochlorides of amines, and cellulose by alkali salts of the disulphonic acids of compounds containing one or more azo groups. Methylene-blue is uncertain, owing probably to its containing sulphur. The membrane probably consists of cellulose, hydrocellulose, and oxycellulose in equilibrium, the two former generally predominating. E. M. C.

Nature and Amount of Substances Capable of Hydrolysis by Invertase and by Emulsin contained in Seeds of some *Leguminosæ*. H. Hérissey and R. Sibassié (*Compt. rend.*, 1924, **178**, 884—886).—Seeds of numerous species of *Leguminosæ* were examined. Reducing sugars were not detected and, if present, formed not more than 0·4% of the dry seeds. Aqueous extracts showed different degrees of dextrorotatory power, which was much diminished by the action of invertase; it is inferred that polysaccharides of strong dextrorotatory power are present. Stachyose was isolated from seeds of fenugreek, Provence lucerne, [illegible] *Indigofera*, and raffinose from those of *Anthyllis vulneraria* and [illegible] sainfoin. Sucrose was present in the majority of the seeds, [illegible] Constantinople acacia and in Indian liquorice (*Abrus* [illegible] for the first time. Indications of [illegible] with purple broom and *Copaifera officinalis*.

Results obtained in the biological determination of comparative amounts of polysaccharides in thirty varieties of *Phaseolus vulgaris*, six of *Pisum sativum*, and four of *Ervum lens* show that the use of invertase for this purpose is satisfactory. H. J. E.

New Crystalline Chromogen, Esculetol, extracted from Horse Chestnuts. G. Bertrand and (Miss) Y. Djoritch (*Compt. rend.*, 1924, **178**, 1233—1236).—The authors have isolated from the fruit of the horse chestnut the chromogenic substance which occurs in the envelope of the fruit and is colourless while in the living cells, but under the influence of the laccase present rapidly becomes deep yellow when the cell sap is exposed to the air. This chromogen, named *esculetol*, crystallises from aqueous solution in lustrous, colourless prisms, commonly united in rosettes, and, in a vacuum over sulphuric acid, undergoes dehydration to a powder of irregular lamellæ and slender needles, m. p. (Maquenne block) 275—280°. In the air, it undergoes gradual oxidation and assumes a pink colour, and in aqueous solution it is coloured an intense green by ferric chloride and brownish-yellow by absorption of oxygen or by addition of sodium or potassium hydroxide. It reduces iodic acid and gold chloride in the cold, and silver nitrate and copper acetate when heated. It is not a glucoside, and the extent to which it reduces cupro-potassium solution is not increased by previous treatment with dilute acid. T. H. P.

The Isoelectric Points of some Plant Proteins. W. H. Pearsall and J. Ewing (*Biochem. J.*, 1924, **18**, 329—339).—The examination of a representative series of plant proteins shows that the isoelectric point of these compounds is usually about p_H 4·5 or less often about p_H 3·3. Edestin is the only exception. S. S. Z.

Solanine Content of Potatoes. A. Bömer and H. Mattis (*Z. Unters. Nahr. Genussm.*, 1924, **47**, 97—127).—The methods previously described for determining solanine are subjected to a critical examination. Von Morgenstern's method does not give quantitative results, and the solanine obtained by Meyer's method is on an average only 62·2% pure. The solubility of solanine in ether, acetone, alcohol, and in faintly ammoniacal water has been redetermined. Neither dilute acetic acid, ammonia, nor barium hydroxide decompose solanine appreciably. A simplified method of determining the solanine content of potatoes is given, which gives considerably higher results than that of Meyer or that of von Morgenstern. The original must be consulted for details. The solanine content of a large number of potatoes of various kinds grown under specified conditions as to soil and fertiliser, determined by this method, varied between 2 and 10 mg. %. Potatoes with a content of more than 20 mg. % of solanine appear to be unsafe for consumption. The solanine content of potatoes definitely shown to be prejudicial to health has varied between 25·7 and 58·3 mg. %. Unripe potatoes have a considerably greater content of solanine than ripe potatoes of the same variety; small potatoes contain more than large ones. An increase in the solanine content occurs on prolonged exposure of potatoes to the light at the same time as the formation of chlorophyll. No connexion could be traced between the use of artificial fertilisers and the solanine content of the potatoes. When potatoes of high solanine content are used as seed, the resulting crop is of normal solanine content, both as regards tops and tubers. H. C. R.

Surface Tension of Saponin Solutions. H. Wastl.—(See ii, 462.)

Comparative Plant Chemistry. IX. Chemistry of Barks. I. C. Feinberg, J. Herrmann, L. Röglsperger, and J. Zellner (*Monatsh.*, 1924, **44**, 261—276).—Young barks of three species of trees were examined: (1) Field maple (*Acer campestre*, L.); this contained: soluble in light petroleum, 0·56%; ether extract, 1·12%; alcoholic extract, 9·34%; total water-soluble matters, 15·65%; water-soluble mineral matters, 1·11%; tannin, 4·00%; phlobaphens, 3·00%; free acids (as KOH), 1·12%; reducing sugars, trace; sucrose, 1·09%; polysaccharides, 0·55%; total nitrogen, 2·05%; total ash, 11·27%. The light-petroleum extract contained a *phytosterol*, m. p. 128°, [α] −24·7°, and hydrolysis of the fats yielded ceryl alcohol, arachidic acid, and a mixture of other acids. The ether extract contained an *octadecyl alcohol*, m. p. 75°. The tannin, of the approximate formula $(C_{10}H_{12}O_5)_n$, gave protocatechuic acid on fusion with alkali.

(2) Hazel (*Corylus Avellana*, L.) contained: soluble in light petroleum, 4·25%; ether-soluble, 3·45%; alcohol-soluble, 9·34%; total water-soluble, 15·06%; reducing sugars, 2·61%; tannin, 5·23%; free acids (as KOH), 3·96%; polysaccharides, 1·36%; soluble mineral matter, 0·94%; total nitrogen, 0·60%; crude fibre, 48·04%; total ash, 5·97%. The light-petroleum fraction yielded a new substance, $C_{34}H_{60}O_2$, termed *corylol*, colourless needles from alcohol, m. p. 240° (decomp.), which gave a cholestol reaction (*acetyl* derivative, m. p. 102°; *benzoyl* derivative, m. p. 136°; *acetylbromo* derivative, m. p. 115°). Corylol is similar to, but not identical with alnulin (*vide infra*), cerin, and friedelin (cf. Istrati and Ostrogovitch, A., 1899, i, 772); the light-petroleum fraction also yielded a *substance* $(C_{20}H_{36}O_2)$, m. p. 199—200°, which gave a cholestol reaction, and a *wax-alcohol*, m. p. 75°. The ether extract gave a *resin acid*, m. p. 272°, and a *substance* crystallising in needles ($C_{35}H_{60}O_4$?), m. p. 254° (*acetyl* derivative, m. p. 215°), named *coryliresinol*, similar to but differing definitely from corylol.

(3) Grey alder (*Alnus incana*, L.) contained: soluble in light petroleum, 8·97%; ether-soluble, 2·91%; alcohol-soluble, 17·32%; tannins, 9·76%; total water-soluble matters, 27·03%; free acids (as KOH), 1·23%; polysaccharides, 3·15%; total nitrogen, 1·26%; [illegible]%. The light-petroleum fraction afforded long, [illegible] substance ($C_{35}H_{60}O$?) termed *alnulin*, m. p. [illegible] derivative, m. p. 237°; *bromine additive*

product, m. p. 210°). A second crystalline product was also isolated, termed *alniresinol* ($C_{34}H_{58}O_3$?), m. p. 179° (decomp.), which gave a cholestol reaction, *acetyl* derivative, needles, m. p. 258°; it appears to be a resin alcohol. Traces of a third *substance*, $C_{34}H_{60}O_3$, were also obtained, m. p. 210°. F. A. M.

Chemical Composition of the Clandestine. A. Goris (*Compt. rend.*, 1924, **178**, 1203—1205).—The glucoside, clandestinin, of *Lathrea clandestina*, the extraction of which is described, appears to be identical with meliatin. H. J. E.

Comparative Plant Chemistry. VIII. *Chamænerium angustifolium*. K. Püringer (*Monatsh.*, 1924, **44**, 255—260).—The leaves and flowers were examined separately, giving the following results (figures for flowers in brackets): soluble in light petroleum, 4·82% (2·76%); in ether, 4·20% (5·39%); in alcohol, 15·61% (19·77%); total water-soluble, 37·45% (41·04%); water-soluble mineral matter, 5·23% (6·05%); free acids (as KOH), 2·46% (5·32%); reducing sugars, 5·27% (8·47%); tannin, 12·15% (12·67%); phlobaphen, 1·07% (—); total nitrogen, 2·47% (2·26%); protein nitrogen, 2·02% (—); crude fibre, 10·54% (13·53%); ash, 7·70% (6·73%). The general results resemble those obtained with *Knautia* (cf. this vol., i, 816). The plant is used in Russia for adulterating tea. The ether extract contained an amorphous white *substance*, m. p. 256—260° (decomp.), $[\alpha]$ +72·75° in alcohol, which forms an *iodine additive* product, m. p. 118—120°, and an *acetyl* derivative, m. p. 178—180°; it is probably a resin alcohol. The alcoholic plant extract contained small amounts of choline and invert-sugar. F. A. M.

Tissue Fluids of Egyptian and Upland Cottons and their F_1 Hybrid. J. A. Harris, Z. W. Lawrence, W. F. Hoffman, J. V. Lawrence, and A. T. Valentine (*J. Agric. Res.*, 1924, **27**, 267—328).—The osmotic concentration of the leaf-tissue fluid, as measured by the freezing-point depression, is slightly but definitely greater in Egyptian than in Upland cottons. The electrical conductivity and acidity are also greater in the Egyptian cotton; the average p_H values varies from 5·26 to 5·40. The osmotic concentration and electrical conductivity are lower in the hybrid than in either of the parents, but the hydrogen-ion concentration falls between those of the parents. As the season advances, the concentrations of total solutes, ionised solutes, and hydrogen ions decrease whilst the differences between the various types of cotton become more marked. Soil conditions and atmospheric conditions during the period of sampling exert a marked influence on the values; the concentration of total solutes is most affected by these environmental factors. E. M. C.

Histological and Chemical Examination of the Seeds of *Ipomœa hederacea*, Jacquin, and of other Species of *Ipomœa*. H. C. Kassner (*Pharm. J.*, 1924, **112**, 328—331, 357—359).—The seeds of *Ipomœa hederacea*, Jacq., *I. muricata*, Jacq., *I. pes-tigridis*, L., *I. coccinea*, L., *I. pilosa*, Sw., and *I. eriocarpa*, R. Br., all contain a crude resin and a fatty oil as principal constituents. The physical and chemical properties of both these constituents of the different species are given and show that the resins and oils obtained from them were very similar to one another. The seeds of *I. muricata* gave a larger percentage of ether extract after extraction with petroleum spirit, but a smaller quantity of crude resin in the subsequent extraction with alcohol than did those of *I. hederacea*. The seeds of *I. hederacea* contained a larger percentage of the medicinally active resin than those of any of the other species. About 2% of a true resin was isolated from the seeds of *I. hederacea* free from glucosidal matter. The crude resin comprises a mixture of this true resin with a large quantity of glucosidal matter and with a saponin-like substance. Neither the true resin nor the crude resin is identical with convolvulin, the ether-insoluble resin of jalap. The true resin and the crude resin of Kaladana (*I. hederacea*) differ from the jalap and scammony resins in that they are insoluble in ether and give an immediate turbidity on acidifying a boiled alkaline ethereal solution. True Kaladana resin is not precipitated as readily or completely as certain other convolvulaceous resins when its alcoholic solution is poured into water. The true, glucoside-free resin of Kaladana possesses medicinal properties similar to those of jalap resin. The crude resin does not, however, form a wholly satisfactory substitute for jalap resin owing to the presence of a large amount of glucosidal matter which acts as a hygroscopic diluent. The percentage of fatty oils and crude resins in the various species of seeds was 9·23—14·94% and 9·20—15·98%, respectively. *I. coccinea* gave the greatest yield of oil and *I. hederacea* the greatest yield of resin. The monographs on Kaladana in the B.P., 1914, and B.P. Codex, 1923, are inaccurate and need revision. H. C. R.

Chemical Factors determining the Quality of Tobacco. V. GRAHAM and R. H. CARR (*J. Amer. Chem. Soc.*, 1924, **46**, 695—702).—There is a relation between the grades of tobacco and their relative solubilities; a high quality cigar tobacco, for instance, has a lower percentage of extractives and nicotine than has a poorer grade. The irritant effect produced by inferior tobaccos is due to the presence of waxes, volatile oils, and loosely combined nicotine, and it is suggested that the quality could be improved by a preliminary extraction with light petroleum. The quality of the tobacco is not so much altered by the use of fertilisers as by changes in the nature of the soil and climatic conditions; of the fertilisers employed superphosphate was found to have the most marked effect in improving the quality. Plants grown on soil containing much lime contained a considerable amount of nicotine-calcium compounds. The best qualities of tobacco are grown on relatively poor sandy and clay soils unsuited for cereals. C. J. S.

Comparative Plant Chemistry. VII. *Knautia silvatica*. [illegible] (*Monatsh.*, 1924, **44**, 247—251).—The leaves and flowers were examined separately and had the following contents (figures for petals in brackets): soluble in light petroleum, 3·21% (2·18%); in ether, 2·13% (3·59%); in alcohol, 25·77% (30·14%); total water-soluble, 40·99% (39·43%); water-soluble mineral matter, 8·27% (6·10%); phlobaphen, 4·68% (6·18%); tannin, 7·80% (6·85%); free acid (as KOH), 2·51% (2·50%); reducing sugars, 4·43% (5·38%); soluble carbohydrates, 4·03% (2·23%); crude fibre, 14·19% (17·37%); pentosans, 7·68% (10·49%); methylpentosans, 1·02% (1·37%); total nitrogen, 1·96% (2·69%); total ash, 13·42% (8·56%). The tannin yielded protocatechuic acid on fusion with potassium hydroxide; invert-sugar and choline were also present in the alcohol extracts from the leaves. The colloidal carbohydrate contained in the aqueous extract yielded mucic acid and furfuraldehyde as degradation products, and is therefore regarded as a galactopentosan. Attention is directed to the similarity in chemical composition of the leaves and petals.

F. A. M.

Chemistry of Heterotropic Phanerogams. IV. J. Einleger, J. Fischer, and J. Zellner (*Monatsh.*, 1924, **44**, 277—295).—Mistletoe (*Viscum album*, L.) gave the following results per 100 parts of dried substance (figures for leaves and young stems are given first and figures for berries in brackets): soluble in light petroleum, 5·13% (5·12%); ether-soluble, 3·26% (2·59%); alcohol extract, —, (41·59%); total water-soluble matter, 37·52% (68·08%); water-soluble mineral matter, 7·79% (5·28%); free acids (as KOH), —, (1·19%); reducing sugars, 0·62% (1·33%); pectins 2·05%; soluble polysaccharides, —, (22·4%); tannin, nil (nil); total nitrogen, 2·30% (2·05%); crude fibre, 20·43% (10·85%); ash, 10·40% (5·51%); soluble pentosans, —, (6·58%); insoluble pentosans, —, (3·47%); methylpentosans, —, (0·89%). A new resin alcohol, *visciresinol*, $C_{15}H_{26}O_2$, decomp. 274—276°, was isolated from the leaves and stem; it adds on bromine and iodine in acetic acid and can be acetylated; choline was present but phlobaphens were absent. The berries contained a viscous product which after hydrolysis gave a *substance* decomposing above 280° (*acetyl* derivative, m. p. 250°), possibly identical with visciresinol; a crystalline *wax-alcohol*, m. p. 71°, was also isolated, and an amorphous resin identical with Reinsch's viscin (cf. *Chem. Zentr.*, 1861, 148).

Loranthus europæus gave the following analysis per 100 parts of dried berries: soluble in light petroleum, 11·38%; ether-soluble, nil; total water-soluble matter, 48·84%; water-soluble mineral matter, 4·28%; free acids (as KOH), 1·44%; reducing sugars, 20·00%; water-soluble polysaccharides, 5·09%; total nitrogen, 2·57%; crude fibre, 15·83%; total ash, 4·60%. The fatty portions of the leaf extracts yielded *loranthyl alcohol*, $C_{24}H_{50}O$, m. p. 71—72° (*acetyl* derivative, m. p. 57—58°, *benzoyl* derivative, m. p. 56—57°). A saturated *hydrocarbon*, $C_{30}H_{62}$, was also isolated, m. p. 65°; carotin and phlobaphens were present. Notable amounts of tannin were present which yielded protocatechuic acid on alkali fusion. The berries after extraction and hydrolysis yielded cetyl alcohol; an amorphous *resin*, $(C_{10}H_{18}O)_x$, was also obtained, m. p. 65—66°, $[\alpha]$ $+14\cdot5°$, giving an *acetyl* derivative, m. p. 70—72°. A comparison of the stems of the parasites and their hosts confirmed the results previously found in other cases (cf. Zellner, A., 1920, i, 131) that the parasites had a higher water-content and contained more free acids and soluble nitrogenous compounds than the host, but considerably less reducing sugars. F. A. M.

Microbiological Analysis of Soil as an Index of Soil Fertility. VII. Carbon Dioxide Evolution. S. A. Waksman and R. L. Starkey (*Soil Sci.*, 1924, **17**, 141—161).—Methods are described for the measurement of carbon dioxide production in soil. The rate at which soils produce carbon dioxide is suggested as a basis on which soils may be classified, both as to fertility and to number of micro-organisms present. For normal soils, carbon dioxide production was greatest where the percentage of organic matter was high, although no direct proportionality was observed. The rate of evolution of carbon dioxide from acid soils was increased by liming, and in these cases nitrification was increased to an even greater extent. A. G. P.

Oxidation of Ammonia and Nitrites by Micro-organisms under Different Conditions. R. N. Gawda (*Soil Sci.*, 1924, **17**, 57—63).—Marked increases in the rates of oxidation of sodium nitrite and ammonium sulphate in culture solutions of nitrifying organisms were observed when an air current was drawn through the liquid. This rate was further considerably increased by allowing the solution to drip through a column of broken limestone on the surface of which a culture of the organisms was established and through which an air current was passed. Nitrite-bacteria were most active in media with p_H 8·0 and nitrate-forming organisms with p_H 8·5—8·8. Magnesium carbonate used as a base during ammonia oxidation proved devoid of toxic effects. A. G. P.

Sulphur Oxidation in Oregon Soils. W. V. Halversen and W. B. Bollen (*Soil Sci.*, 1923, **16**, 479—490).—Attempts to correlate factors concerned in the use of sulphur as a fertiliser are described. An approximate proportionality was found between the sulphur-oxidising power of soils and their sulphate contents. The total sulphur content of soils bore no apparent relationship to either the sulphur-oxidising power or the sulphate content. The rate of sulphur-oxidation can be increased by a previous treatment with sulphur and by the use of inoculated sulphur. Oxidation was favoured by aëration and temperature increases. In heavy soils with high buffer capacities, sulphur oxidation was considerably slower than in light sandy soils having small buffer [illegible] The sulphur-oxidising power of a soil was in no way [illegible] hydrogen-ion concentration. A. G. P.

Biochemical Conditions of a Soil treated with Different Organic Manures. E. HASELHOFF and O. LIEHR (*Landw. Versuchs.-Stat.*, 1924, **102**, 43—59). **Carbon Dioxide Content of the Soil Atmosphere.** E. HASELHOFF and O. LIEHR (*ibid.*, 60—72). **Nitrogen Economy of Arable Soil.** E. HASELHOFF (*ibid.*, 73—89). **Ammonia and Nitric Acid Content of the Soil.** E. HASELHOFF and F. HAUN (*ibid.*, 90—103). **Effect of Fallow, Dung, and Green Manures in Conjunction with Mineral Manures.** E. HASELHOFF (*ibid.*, 104—121).—This series of papers contains a detailed discussion of an investigation of the soil from a large number of plots, over a period of 10 years, on which a rotation of wheat, potatoes, rye, and oats followed green manuring with serradella, peas, and clover. Other plots received dung or were fallowed. The whole rotation was repeated twice. Determinations are recorded of bacterial numbers, and ammonifying, nitrifying, and nitrogen-fixing powers of soil samples; the carbon dioxide content of the soil atmosphere at depths of 25 and 50 cm.; the total nitrogen recovered in the crops; the ammonia and nitric acid of the soil, as determined colorimetrically in aqueous extracts; and the crop yields with green manures and ammonium sulphate. Reference should be made to the original papers, since the results do not allow any definite conclusions to be given briefly.
E. M. C.

Moisture Relationships in an Ideal Soil. B. A. KEEN (*J. Agric. Sci.*, 1924, **14**, 170—177).—The views of a number of soil physicists are discussed in a theoretical paper, on the basis of the mathematical relationships of soil and water in an ideal soil.
A. G. P.

Imbibitional Soil Moisture. E. A. FISHER (*J. Agric. Sci.*, 1924, **14**, 204—220).—In continuation of former papers (see *Ann. Repts.*, 1923, **20**, 202), the nature of imbibitional or "gel" water is discussed, particularly in respect of its effect on the movement of water in soils. The imbibitional process may be due to the attainment of a Donnan equilibrium within the "swollen" colloidal particles of the soil. The possible effects of imbibition on the movement of soil-water are discussed mathematically. A. G. P.

Measurement of Hydrogen-ion Concentration in Soil by means of the Quinhydrone Electrode. E. BILLMANN (*J. Agric. Sci.*, 1924, **14**, 232—239).—Apparatus is described for the determination of hydrogen-ion concentrations of soil–water suspensions by means of an electrode vessel containing quinhydrone as the source of hydrogen. Rapid equilibrium is attained, and the results are in close agreement with those yielded by the colorimetric method and the standard hydrogen electrode. A. G. P.

Electrical Conductivity of Extracts from Soils of Various Types and its Use in Detecting Infertility. W. R. G. ATKINS (*J. Agric. Sci.*, 1924, **14**, 198—203).—The electrical conductivity of aqueous soil extracts increased with the period of extraction in the case of rich soils, but reached its maximum quickly in the case of infertile soils and peats. High conductivity does not necessarily indicate a good soil, but a rapid increase with extended extraction period appears to be characteristic of fertility. A. G. P.

Modifications in Soil Dried in the Air. A. LEBEDIANTZEV (*Compt. rend.*, 1924, **178**, 960—963).—The proportions of organic matter, total nitrogen, and ammoniacal nitrogen extractable from soil by water and acid solutions are greatly increased by preliminary drying of the soil in the air. At the same time, the extractable phosphoric acid increases appreciably and the extractable mineral matter slightly, whilst the bacteria present undergo considerable diminution. These effects are due, not to the action of oxygen or light, but to the loss of water and to the rise of temperature caused by the sun's rays. T. H. P.

Determination of Carbonic Acid present as Carbonate in Soils. P. B. SANYOL (*Agric. Res. Inst. Pusa, Bull.* No. 151).—Carbonates in the soil are decomposed by treatment with cold hydrochloric acid in a vessel containing a stirrer. When no more gas is evolved the carbon dioxide dissolved in the liquid is completely driven out by the generation of hydrogen from aluminium foil. The rate of hydrogen generation is regulated by the addition of a copper sulphate solution. A. G. P.

Calcium Content of Soil in Relation to Absolute Reaction. C. O. SWANSON, P. L. GAINEY, and W. L. LATSHAW (*Soil Sci.*, 1924, **17**, 181—191).—Analyses of a large number of soils indicate that in similar types of soil a close relationship exists between the p_H value of the soil and the amount of calcium present in a form soluble in cold *N*-hydrochloric acid solution. A. G. P.

Adsorption and Absorption of Bases by Soils. C. P. JONES (*Soil Sci.*, 1924, **17**, 255—273).—Experiments are described in support of the view that the adsorption of bases by soil colloids is but a preliminary or accessory factor to the absorption of bases, which is a chemical reaction between the soil constituents and added substances. The latter phenomenon is considered of the greater importance and is governed by the chemical nature of the reactive soil constituents and by those factors limiting the extent of the hydrolysis of the reacting substance. The absorption of basic ions is greater as the degree of ionisation decreases. The absorption of the base of sparingly soluble substances is dependent on their fineness of division. A. G. P.

Organic Chemistry.

Refractive Indices of Hexanes and Hexenes. H. van Risseghem (*Bull. Soc. chim. Belg.*, 1924, **33**, 115—119; cf. A., 1922, i, 313).—The following corrected values are given. ββ-Dimethylbutane, n_D^{15} 1·3716, $n_{H\beta}^{15}$ 1·3762, $n_{H\gamma}^{15}$ 1·3801; *iso*hexane, $n_{H\alpha}^{15}$ 1·3725, $n_{H\beta}^{15}$ 1·3792, $n_{H\gamma}^{15}$ 1·3829; γ-methylpentane, n_D^{15} 1·3793, $n_{H\beta}^{15}$ 1·3841, $n_{H\gamma}^{15}$ 1·3878; βγ-dimethylbutane, $n_{H\beta}^{15}$ 1·3855, $n_{H\gamma}^{15}$ 1·38935.

H. J. E.

Photochlorination of Aliphatic Compounds in Carbon Tetrachloride. A. Benrath and E. Hertel (*Z. wiss. Phot.*, 1924, **23**, 30—40).—The amount of chlorine dissolved in technical or in pure carbon tetrachloride (Kahlbaum) continuously diminishes when the solution is subjected to the action of light. If, however, the carbon tetrachloride has been previously subjected at its boiling point to the prolonged action of chlorine and then purified by treatment with nitric acid followed by sodium carbonate and chlorine again dissolved in it, the chlorine titre no longer diminishes but increases when the solution is subjected to light. Perfectly purified and dried carbon tetrachloride was shown to contain free chlorine after several days' exposure to light. The amount of decomposition is not sufficiently great to hinder the use of carbon tetrachloride as a medium in which to study the photochlorination of various aliphatic compounds. The chlorine solutions employed contained about 0·05 g. of chlorine in 10 g. of solution. In some of the compounds investigated, one atom of hydrogen was displaced, in others two. The reaction was generally preceded by an induction period. The amount of chlorination, in some cases, was proportional to the time and in others to the logarithm of the time. If two atoms of hydrogen are displaced, the reaction takes place in distinct steps. The second displacement frequently takes place with a rapidity much greater than that at the end of the first, and is preceded by a new induction period. Chloroform, after an induction period of about 30 mins., absorbs about 70% of the chlorine required for its conversion into carbon tetrachloride. The reaction is not reversible. Tetrachloroethane was not attacked by chlorine in 3 hours. Acetic acid was converted into monochloroacetic acid with very little tendency for the reaction to proceed further. Acetyl chloride and *iso*butyric acid behave similarly to acetic acid. With propionic acid and ethyl malonate the reaction commenced slowly and then continued at a rate proportional to the time until one atom of hydrogen was displaced. The second atom reacted at a much slower rate and in accordance with the logarithmic law. Two atoms of hydrogen were displaced in the case of *n*-butyric acid, both at the logarithmic rate, the two steps of the reaction being markedly distinct. The chlorination of ethyl ether proceeded linearly during the displacement of one atom, then, after a slowing up, a second atom was displaced at the logarithmic rate. The induction period was long in the case of acetic anhydride and the reaction was in two phases, but the rate was neither linear nor according to the logarithmic law. A. C.

***tert*.-Butyl Alcohol.** R. R. READ and F. PRISLEY (*J. Amer. Chem. Soc.*, 1924, **46**, 1512—1515).—The vapour of *iso*butyl alcohol is passed over pumice coated with aluminium oxide, contained in an iron tube, at 500—520°, and the *iso*butylene formed is freed from water and unchanged alcohol, and hydrated to *tert*.-butyl alcohol by absorption in 50% sulphuric acid, either directly or from its solution in kerosene. The yield is improved by using a glass catalyst tube at 450—475°. The use of phosphoric acid on coke as the dehydrating catalyst (cf. King, T., 1919, **115**, 1404), even at 210—230°, led to the loss of half the total hydrocarbon by polymerisation. F. G. W.

Preparation of Dialkylethinenyl Carbinols. R. LOCQUIN and S. WOUSENG (*Bull. Soc. chim.*, 1924, [iv], **35**, 597—604; cf. A., 1922, i, 617).—The sodium derivatives of ketones may be obtained with a minimum of condensation by-reactions by adding finely-powdered sodamide gradually to a mixture of the ketone (1 part) and dry ether (4—5 parts) kept thoroughly agitated and cooled for several hours, the ammonia being removed under reduced pressure. γ-Ethyl-Δ^{α}-pentinene-γ-ol, $OH\cdot CEt_2\cdot C{:}CH$, obtained from sodium diethyl ketone and acetylene by the method previously described, forms an *allophanate*, $Et_2C(C{:}CH)O\cdot CO\cdot NH\cdot CO\cdot NH_2$, fine needles, m. p. 130—131°. *γζ-Diethyl-Δ^{δ}-octinene-γζ-diol*, $OH\cdot CEt_2\cdot C{:}C\cdot CEt_2\cdot OH$, m. p. 76°, b. p. 132—135°/14 mm., is formed in small quantity along with the ethinenylcarbinol. On distillation with a little solid potassium hydroxide, it is decomposed quantitatively into acetylene and diethyl ketone. α-*cyclo*Hexyl-Δ^{α}-propinene-γ-ol has m. p. 22°, b. p. 73—75°/15 mm.; *allophanate*, m. p. 197°. *ζ-Methyl-γ-*iso*butyl-Δ^{α}-heptinene-γδ-diol*, $C_4H_9\cdot CH(OH)\cdot C(OH)(C_4H_9)\cdot C{:}CH$, has m. p. 101—102°. *α-Phenyl-γ-propyl-Δ^{α}-hexinene-γ-ol*, $PhC{:}C\cdot CPr_2\cdot OH$, b. p. 153—158°/10 mm., is obtained by the action of phenylacetylene on the sodium derivative of dipropyl ketone. F. G. W.

Methylpropylethinenylcarbinol [γ-Methyl-Δ^{α}-hexinene-γ-ol] and its Derivatives. R. LOCQUIN and S. WOUSENG (*Bull. Soc. chim.*, 1924, [iv], **35**, 604—606).—*γ-Methyl-Δ^{α}-hexinene-γ-ol*, $OH\cdot CMePr\cdot C{:}CH$, obtained by the action of acetylene on sodium methyl *n*-propyl ketone, has b. p. 137°; *allophanate*, m. p. 133°. *δη-Dimethyl-Δ^{ϵ}-decinene-δη-diol*, $OH\cdot CMePr\cdot C{:}C\cdot CMePr\cdot OH$, m. p. 60°, b. p. 130—135°/10 mm., is formed in small quantity along with the carbinol. The latter substance combines with water in presence of acid mercuric sulphate with formation of *γ-methylhexan-γ-ol-*β*-one*, b. p. 166—168° (*semicarbazone*, m. p. 163—164°). F. G. W.

Action of Acetylene on Sodium Compounds of Ketones. Isomeric Transformation of Dialkylvinylcarbinols into ββ-Dialkylallyl Alcohols. S. Wouseng (*Ann. Chim.*, 1924, [x], 1, 343—416).—The sodium compound of a ketone, obtained by using sodamide, reacts in ethereal suspension with acetylene under a water-pressure of 500—600 cm. to yield an acetylenic alcohol (cf. Locquin and Wouseng, A., 1922, i, 617, 710; 1923, i, 302). Pinacolin thus affords *methyl*-tert.-*butylethinenylcarbinol* [γδδ-*trimethylpentinene-γ-ol*], $CMe_3\cdot CMe(OH)\cdot C\vdots CH$, an oil with a mint-like odour, b. p. 144°, d_4^{11} 0·8806, n_D^{11} 1·4441; this forms a crystalline *hydrate* of low m. p., an *allophanate* (cf. Behal, A., 1919, ii, 301), needles, m. p. 156° (after drying at 110°), and an *acetate*, b. p. 156—159°. Two, or three, by-products, all presumably stereoisomeric forms of the *glycol*, $CMe_3\cdot CMe(OH)\cdot C\vdots C\cdot CMe(OH)\cdot CMe_3$ (cf. Dupont, A., 1914, i, 134), are also formed, the viscous oily mixture of b. p. 148—150°/14 mm. being separable into scales, m. p. 88—89°, rhomboidal tablets, m. p. 78°, and another substance (?), m. p. 67—68°. The saturated alcohol, *methylethyl*-tert.-*butylcarbinol*, obtained from the acetylenic compound by treatment with hydrogen in presence of platinum black, or directly from pinacolin and magnesium ethyl iodide, has b. p. 152°, and yields an *allophanate*, m. p. 134—135°. Partial hydrogenation of the acetylenic compound to the ethylenic alcohol, *methyl*-tert.-*butylvinylcarbinol*,

$$CMe_3\cdot CMe(OH)\cdot CH{:}CH_2,$$

b. p. 144—146°, d_4^{11} 0·8576, n_D^{11} 1·4452, which also possesses a strong mint-like odour, was best effected by the action of hydrogen in presence of reduced nickel (in methyl-alcoholic solution). This substance also forms a *hydrate* of low m. p. and gives an *allophanate*, needles, m. p. 167—168° (decomp.). When treated with acetic anhydride at 140°, or boiling glacial acetic acid, it undergoes a molecular transformation analogous to that of linalool into geraniol and nerol (Forster and Cardwell, T., 1913, **103**, 1338 etc.), thus demonstrating (cf. also the results described below) that this change is a general one for tertiary vinylcarbinols. The primary alcohol so obtained, γδδ-*trimethyl*-Δ^β-*pentenol*, separated as the hydrogen phthalate (cf. Stephan, A., 1899, i, 68), has b. p. 84°/12 mm., and yields an *allophanate*, m. p. 180—181°. When it is oxidised by a chromic–sulphuric acid mixture, or by atmospheric oxygen and metallic silver, it is converted into βγγ-*trimethyl*-Δ^α-*pentenaldehyde*, b. p. 75—78°/15 mm., the *semicarbazone* of which has m. p. 204—205°. This aldehyde is also obtained by direct oxidation of the above ethylenic alcohol, γδδ-trimethyl-Δ^β-pentenol, by chromic-sulphuric acid, in a manner exactly analogous to the formation of geraniol and citral from linalool. Further oxidation affords the *acid*, $CMe_3\cdot CMe{:}CH\cdot CO_2H$, m. p. 85—86°, which when treated with warm 80% sulphuric acid is converted into the *lactone* of γγ-*dimethyl*-β-*hydroxymethylvaleric acid* (cf. Petshnikoff, A., 1902, i, 338), which is also obtained when *ethyl* γγ-*dimethylvalerate*, b. p. 96—99°/10 mm., prepared from pinacolin and ethyl bromoacetate, is heated with formic acid, no dehydration to the corresponding derivative of acrylic acid taking place in this case.

Dipropyl ketone, treated with sodamide and acetylene, yields *γ-propyl-Δ^{α}-hexinen-γ-ol*, $CPr^{\alpha}_2(OH)\cdot C\vdots CH$, b. p. 69—71°/12 mm., d_4^{11} 0·8691, n_D^{11} 1·4443, the *acetyl* derivative of which has b. p. 82—83°/10 mm., and the *allophanate*, m. p. 143°. As a by-product, the glycol, $CPr_2\cdot C(OH)\cdot C\vdots C\cdot C(OH)\cdot CPr_2$ (Dupont, *loc. cit.*), is formed. By reduction as described above, ethyldipropylcarbinol (Tschebotarev and Saytzev, A., 1886, 437) is formed, whilst partial reduction affords *dipropylvinylcarbinol*, b. p. 75—76°/12 mm., the *allophanate* of which has m. p. 102—103°. When this ethylenic tertiary alcohol is boiled with acetic acid and the product saponified, the primary isomeride is obtained, exactly as described above; purified through its hydrogen phthalate, *γγ-dipropylallyl alcohol* has b. p. 99—101°/12 mm., and gives an *allophanate*, m. p. 147—148°. When reduced with hydrogen and platinum black, it yields *γ-propylhexyl alcohol*, b. p. 107—108°, which yields an *allophanate*, needles, m. p. 133—134°, and a *pyruvic* ester, b. p. 140—145°/20 mm., the *semicarbazone* of which has m. p. 116—117°. This saturated alcohol is identical in all respects with that obtained by condensing butyrone with ethyl bromoacetate (by the Grignard reaction), dehydrating the product, *ethyl β-hydroxy-β-propylhexoate*, b. p. 160—165°/85 mm., by heating with formic acid and reducing the resulting *ethyl β-propyl-Δ^{α}-hexenoate*, b. p. 122—128°/30 mm., with sodium and alcohol. *β-Propyl-Δ^{α}-hexenaldehyde* is obtained by regulated oxidation either of γ-propylhexenol, or of the parent dipropylvinylcarbinol; it has b. p. 75—76°/12 mm., and gives a semicarbazone, m. p. 171—173°.

ζ-Methyl-β-heptanone (Bouveault and Locquin, A., 1905, i, 18) yields γη-dimethyloctinene-γ-ol, $CHMe_2\cdot[CH_2]_3\cdot CMe(OH)\cdot C\vdots CH$, which has b. p. 187—188°, or 83—85°/10 mm.; this gives an *allophanate*, needles, m. p. 114—115°. Stereoisomeric *glycols* are produced as by-products and are isolated first as an oil of b. p. 183—184°/12 mm., from which crystals of m. p. 66—68° may be separated, and the second component forms the main proportion of a pasty mass melting at about 35°. βζ-Dimethyloctan-ζ-ol, identical with Barbier and Locquin's preparation (A., 1914, i, 833), is obtained by reduction of the acetylenic derivative, whilst regulated reduction produces *methyl*iso*hexylvinylcarbinol*, b. p. 89—91°/15 mm., which, like its analogues, is readily converted by treatment with hot acetic acid, and subsequent purification through the hydrogen phthalate, into *γη-dimethyl-Δ^{β}-octen-α-ol*, $CHMe_2\cdot[CH_2]_3\cdot CMe{:}CH\cdot CH_2\cdot OH$, b. p. 110°/12 mm. When this is reduced, a tetrahydrogeraniol is formed, the allophanate of which has m. p. 117°, the pyruvate, b. p. 140—145°/12 mm., and the semicarbazone of the latter, m. p. 118°. This tetrahydrogeraniol was identical with the product obtained via ethyl β-hydroxy-βζ-dimethyloctoate (cf. Bouveault and Blanc, A., 1905, i, 11). *Dihydrocitral*,

$$CHMe_2\cdot[CH_2]_3\cdot CMe{:}CH\cdot CHO,$$

obtained by oxidising either the vinylcarbinol or its primary isomeride, yields a *semicarbazone*, m. p. 164°. The above results show that no conclusion can be drawn from the results of a chromic-sulphuric acid oxidation as to the presence of a primary alcoholic grouping; catalytic oxidation, on the other hand, gives trustworthy results. The author discusses the mechanism of these isomeric transformations and describes experiments which indicate that Tiemann's explanation (A., 1894, i, 83) is unsatisfactory. W. A. S.

Constitution of Farnesol. Synthesis of Dihydrofarnesol, a new Aliphatic Sesquiterpene Alcohol. A. VERLEY (*Bull. Soc. chim.*, 1924, [iv], **35**, 606—608).—Farnesal, obtained by the oxidation of farnesol with chromic acid, yields, on boiling with 10% potassium carbonate solution, acetaldehyde and dihydro-ψ-ionone, and on reducing the glycidic ester of this compound or that of ψ-ionone with sodium and amyl alcohol, *dihydrofarnesol*,

$$CH_2{:}CMe{\cdot}[CH_2]_3{\cdot}CMe{:}CH{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

is obtained as an oily, amber liquid with an odour of cedar wood. F. G. W.

Stereoisomerism among Trisubstituted αβ-Glycols and the Production of Stereoisomerides by inverting the Order of Introduction of the Substituent Radicals. M. TIFFENEAU and J. LEVY (*Compt. rend.*, 1924, **178**, 1724—1726).—The products obtained by treating ketols of the general formula CHPh(OH)·CO·R with magnesium alkyl bromides, MgR′Br, are different from those formed when MgRBr acts on CHPh(OH)·CO·R′. The former (R being smaller than R′) are provisionally termed α, the latter β. The *α-variety* of *αβ-dihydroxy-α-phenyl-β-methylbutane* has m. p. 85°; the *β-variety*, m. p. 73°. Similarly, the α- and *β-forms* of *αβ-dihydroxy-α-phenyl-β-ethylhexane* have m. p. 88° and 81°, and the α- and *β-ethylhydrobenzoins* have m. p. 105° and 117° respectively. The isomeric forms of these substances yield the same product when dehydrated with concentrated sulphuric acid. W. A. S.

Replacement of Acid Radicals in Glycerides. K. H. BAUER (*Ber.*, 1924, **57**, [*B*], 897—899).—The action of *m*-nitrobenzoyl chloride on glyceryl α-benzoate dissolved in cold chloroform and quinoline (cf. Fischer, A., 1920, i, 808) leads to the production of *glyceryl tri-*m*-nitrobenzoate*, m. p. 160—161° after softening at 158°, in yield which varies with the experimental conditions. H. W.

Preparation of Ethers from Secondary Alcohols by Dehydration with a Sulphonic Acid. R. VERNIMMEN (*Bull. Soc. chim. Belg.*, 1924, **33**, 96—101).—The preparation is easily effected in presence of *p*-toluenesulphonic acid; a high temperature and too great an excess of catalyst should be avoided in order to obviate the formation of ethylenic hydrocarbons. In the aliphatic series, dehydration is more difficult, as the alcohols must be heated nearly to boiling point. The following are described: Di-β-*n*-hexyl ether (cf. Wanklyn and Erlenmeyer, T., 1863, 221), b. p. 200°/760 mm., d_{20}^{20} 0·7889, n_{D}^{20} 1·4152; *di*-β-n-*amyl ether*, b. p. 160—163°/760 mm., d_{20}^{20} 0·7830, n_{D}^{20} 1·4078; di(α-phenyl-α-propyl) ether, b. p. 164°/14 mm., d_{20}^{20} 1·0043, n_{D}^{20} 1·5420 (cf. Oddo and Rosso, A., 1911, i, 443); di(α-phenyl-α-*n*-butyl) ether, b. p. 178—179°/13 mm.,

d^{20}_{20} 0·9769, n^{20}_{D} 1·5275 (cf. Oddo, *loc. cit.*); di(α-*phenyl*-α-n-*amyl*) *ether*, b. p. 199°/14 mm., d^{20}_{20} 0·9574, n^{20}_{D} 1·5175. H. J. E.

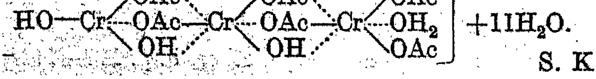
Derivatives of γ-Chloro-*n*-propyl Alkyl Ethers. W. Dulière (*Bull. Soc. chim.*, 1924, [iv], **35**, 584—590).—αγ-Dichloropropyl alkyl ethers (this vol., i, 258) react vigorously with magnesium organohalides with formation of α-substituted γ-chloropropyl alkyl ethers. Of the following compounds described, which are all colourless, strong-smelling oils, the aromatic derivatives are viscous and distil badly under reduced pressure. They are all stable to dilute sodium hydroxide and only slowly attacked by silver nitrate, the mobility of the chlorine atom increasing with increasing molecular weight. γ-*Chloro*-α-*phenyl*-n-*propyl methyl ether*, $Me{\cdot}O{\cdot}CHPh{\cdot}CH_2{\cdot}CH_2Cl$, b. p. 110°/12 mm., d^{20} 1·097, n^{20}_{D} 1·52219; γ-*chloro*-α-*phenyl*-n-*propyl ethyl ether*, b. p. 120°/11 mm., d^{20} 1·066, n^{20}_{D} 1·51502; γ-*chloro*-α-*phenyl*-n-*propyl* n-*propyl ether*, b. p. 130°/12 mm., d^{20} 1·044, n^{20}_{D} 1·50492; γ-*chloro*-α-*phenyl*-n-*propyl* iso*butyl ether*, b. p. 137°/11 mm., d^{20} 1·024, n^{20}_{D} 1·50118; γ-*chloro*-α-*phenyl*-n-*propyl* iso*amyl ether*, b. p. 145°/13 mm., d^{20} 1·019, n^{20}_{D} 1·50212; *methyl* γ-*chloro*-α-*methyl*-n-*propyl ether*, b. p. 35°/10 mm.; *methyl* γ-*chloro*-α-*ethyl*-n-*propyl ether*, b. p. 40°/10 mm., 147°/atmospheric pressure, d^{22} 0·964, n^{22}_{D} 1·42501; *ethyl* γ-*chloro*-α-*methyl*-n-*propyl ether*, b. p. similar, d^{22} 0·971, n^{22}_{D} 1·42751; *methyl* γ-*chloro*-α-iso*propyl*-n-*propyl ether*, b. p. 47°/11 mm., d^{20} 0·951, n^{20}_{D} 1·43096. α-*Benzyl*-n-*propyl methyl ether*, fine white needles, odour of aniseed, m. p. 34°, b. p. 130°/12 mm., d^{74} 0·983, n^{74}_{D} 1·54998, was obtained by the action of magnesium benzyl bromide on methyl αγ-dichloro-*n*-propyl ether, instead of the expected γ-chloro derivative. F. G. W.

Alkyl Ethers of Ethylene Glycol. L. H. Cretcher and W. H. Pittenger (*J. Amer. Chem. Soc.*, 1924, **46**, 1503—1504).—Ethylene oxide or ethylene chlorohydrin (1·1 mols.) is added to a solution of sodium (1 mol.) in the appropriate alcohol, the glycol monoalkyl ether being separated by fractionation after removal of the sodium chloride. *Mono*iso*propyl*, b. p. 144°/743 mm.; *monopropyl*, b. p. 150°/743 mm.; *mono*iso*butyl*, b. p. 158·8°/743 mm.; *monobutyl*, b. p. 170·6°/743 mm., and *monoamyl glycol ether*, b. p. 181°/745 mm., are described. F. G. W.

Manganese Acetate. A. F. G. Cadenhead and W. H. Vining (*Can. Chem. Met.*, 1924, **8**, 64—65).—Manganese acetate, $Mn(OAc)_2,4H_2O$, rose-pink plates or flat, monoclinic prisms, dissolves to the extent of 64·5 g. in 100 g. of water at 5°.

Chemical Abstracts.

Space Significance of the Co-ordination Number in Polynuclear Compounds. II. Constitution of the Violet Chromic Acetate. H. Reihlen (*Z. anorg. Chem.*, 1924, **133**, 82—90; cf. A., 1921, ii, 193).—The violet chromic acetate is considered to be a compound of co-ordination number 10 :—



$$\left[HO{-}Cr\begin{matrix}OAc\\OAc\\OH\end{matrix}{-}Cr\begin{matrix}OAc\\OAc\\OH\end{matrix}{-}Cr\begin{matrix}OAc\\OH_2\\OAc\end{matrix}\right]+11H_2O.$$

S. K. T.

Electrolysis of Mixtures of Acetates and Trichloroacetates. R. E. GIBSON (*Proc. Roy. Soc. Edin.*, 1924, **44**, 140—152).—In the electrolysis of an aqueous solution of potassium acetate and trichloroacetate containing 2 mols. of the former salt to 1 mol. of the latter, the main products are those from single molecules of either acid, namely, ethylene, formaldehyde, and hydrochloric acid. Smaller amounts of derivatives from 2 mols. of either acid, namely, ethane, trichloromethyl trichloroacetate, and hexachloroethane, and from 1 mol. of each acid, trichloromethyl acetate, were also obtained. All reactions resulted in the liberation of carbon dioxide, whilst the formation of carbon monoxide was also observed. A. COUSEN.

Action of Acetic Anhydride on Hydrated Metallic Salts. "Acetylated" Salts. A. RECOURA (*Compt. rend.*, 1924, **178**, 2217—2221).—The action of acetic anhydride on certain hydrated metallic salts is primarily one of dehydration which, in some cases, is complete, but in others certain molecules of water remain combined with the salt and by means of their residual valencies attack molecules of the anhydride. The anhydrous salts do not combine with acetic anhydride. The acetylated salts are generally only stable in an atmosphere of acetic anhydride, and in air rapidly lose their acetic anhydride and unite with water to form the original hydrated salt. The acetylated salt which has lost some acetic anhydride by short exposure to air slowly recombines with it to form the normal acetylated salt when replaced in an atmosphere of the acetic anhydride. When placed over quicklime in a desiccator, they lose the whole of their acetic anhydride but retain their water, so that the anhydride is not combined with the water in the form of acetic acid. Copper sulphate yields the *compound* $CuSO_4,H_2O,Ac_2O$. Nickel sulphate yields the *compound* $NiSO_4,H_2O,2Ac_2O$, which on placing in a desiccator over quicklime loses only 1 mol. of acetic anhydride, leaving the *compound* $NiSO_4,H_2O,Ac_2O$. Magnesium sulphate yields the *compound* $MgSO_4,1{\cdot}3H_2O,2Ac_2O$ which also loses only 1 mol. of acetic anhydride by the action of quicklime. J. W. B.

Salts of *iso*Valeric Acid and α-Bromo*iso*valeric Acid with Organic Bases. H. GOLDSCHMIDT and O. NEUSS (D.R.-P. 386616; from *Chem. Zentr.*, 1924, i, 1713).—It is claimed that neutral salts of diethylenediamine with *iso*valeric acid and α-bromo*iso*valeric acid may be prepared. *Diethylenediamine* iso*valerate* has m. p. 136°. *Diethylenediamine α-bromo*iso*valerate* sinters at 136° and decomposes at higher temperatures. G. W. R.

Synthesis of Normal Fatty Acids from Stearic Acid to Hexacosanoic Acid. P. A. LEVENE and F. A. TAYLOR (*J. Biol. Chem.*, 1924, **59**, 905—921).—The syntheses were carried out by the series of reactions: $R{\cdot}CO_2R \longrightarrow R{\cdot}CH_2{\cdot}OH \longrightarrow R{\cdot}CH_2I \longrightarrow R{\cdot}CH_2{\cdot}CN \longrightarrow R{\cdot}CH_2{\cdot}CO_2H$. The following compounds are recorded: Ethyl stearate, m. p. 32·5—33·5°; b. p. 152°/0·18 mm. *Ethyl* n-*nonadecoate*, m. p. 37—38°; b. p. 166—

168°/0·27 mm. *Ethyl* n-*eicosoate*, m. p. 41·5—42·5°; b. p. 177°/0·28 mm. *Ethyl* n-*heneicosoate*, m. p. 45—46°. *Ethyl* n-*docosoate*, m. p. 48·5—49·5°; b. p. 184—185°/0·20 mm. *Ethyl* n-*tricosoate*, m. p. 52—53°; b. p. 198—199°/0·27 mm. *Ethyl* n-*tetracosoate*, m. p. 55·5—56·5°; b. p. 198—199°/0·24 mm. *Ethyl* n-*pentacosoate*, m. p. 58—59°; b. p. 216—217°/0·50 mm. Methyl stearate, m. p. 38·5—39·5°. *Methyl* n-*nonadecoate*, m. p. 39·5—40·5°. *Methyl* n-*eicosoate*, m. p. 46—47°. *Methyl* n-*heneicosoate*, m. p. 48—49°. *Methyl* n-*docosanoate*, m. p. 53—54°. *Methyl* n-*tricosoate*, m. p. 55—56°. *Methyl* n-*tetracosoate*, m. p. 59—60°. *Methyl* n-*pentacosoate*, m. p. 61—62°. n-*Nonadecanol*, m. p. 62—63°; b. p. 166—167°/0·32 mm. n-*Eicosanol*, m. p. 65·5—66·5°; b. p. 178°/0·40 mm. n-*Heneicosanol*, m. p. 68—69°. n-*Docosanol*, m. p. 70·5—71·5°; b. p. 180°/0·22 mm. n-*Tricosanol*, m. p. 73·5—74·5°; b. p. 191—193°/0·7 mm. n-*Tetracosanol*, m. p. 76·5—77·5°; b. p. 210—210·5°/0·40 mm. n-*Pentacosanol*, m. p. 78·5—79·5°; b. p. 214—216°/0·36 mm. n-*Octadecyl iodide*, m. p. 34·5—35·5°; b. p. 164°/0·22 mm. n-*Nonadecyl iodide*, m. p. 42·5—43·5°; b. p. 174—174·5°/0·22 mm. n-*Eicosyl iodide*, m. p. 42—43°. n-*Heneicosyl iodide*, m. p. 49—50°. n-*Docosyl iodide*, m. p. 48·5—49·5°; b. p. 198°/0·23 mm. n-*Tricosyl iodide*, m. p. 55—56°; b. p. 205°/0·45 mm. n-*Tetracosyl iodide*, m. p. 54·5—55·5°; b. p. 207—209°/0·35 mm. n-*Pentacosyl iodide*, m. p. 60—61°. n-*Octadecyl cyanide*, m. p. 42·5—43·5°. n-*Nonadecyl cyanide*, m. p. 49·5—50·5°. n-*Eicosyl cyanide*, m. p. 48·5—49·5°. n-*Heneicosyl cyanide*, m. p. 55·5—56·5°. n-*Docosyl cyanide*, m. p. 53·5—54·5°. n-*Tricosyl cyanide*, m. p. 61—62°. *n*-Tetracosyl cyanide, m. p. 58—59°. n-*Pentacosyl cyanide*, m. p. 61—62°. Stearic acid, m. p. 70·5—71·5°. n-*Nonadecoic acid*, m. p. 69—70°. n-*Eicosanoic acid*, m. p. 76—77°. n-*Heneicosoic acid*, m. p. 75—76°. *n*-Docosoic (behenic) acid, m. p. 81—82°. n-*Tricosoic acid*, m. p. 80—81°. n-*Tetracosoic acid*, m. p. 85—86°. n-*Pentacosoic acid*, m. p. 84—85°. n-*Hexacosoic acid*, m. p. 88—89°. C. R. H.

Action of Alcoholic Iodine Solutions on Unsaturated Fatty Acids and Fatty Oils. Influence of Water and Potassium Iodide on the Course of the Reaction. B. M. Margosches, W. Hinner, and L. Friedmann (*Ber.*, 1924, **57**, [*B*], 996—1001; cf. this vol., i, 487).—The action of alcoholic iodine solutions on oleic acid is not confined to the alcoholic solution, but proceeds, especially if the period of reaction is short, after diluting the mixture with water preparatory to titrating the excess of iodine; the addition of hypoiodous acid is apparently almost instantaneous at the moment of dilution. The presence of potassium iodide hinders the reaction, probably on account of its tendency to reverse the reaction: $I_2+H_2O \longrightarrow I(OH)+HI$ (cf. also Ingle, A., 1902, i, 528; 1904, ii, 456). Experiments in which the addition of water was omitted, or its influence restricted by the prior addition of carbon tetrachloride, gave lower iodine values after 1 hour's contact with the iodine solution, and it thus appears that the quickening of the reaction is due to the water itself. Similar results were obtained with castor, sesamé, poppy-seed, and linseed oils in alcoholic solution. The free acid liberated in these experiments corresponds with about 50% of the iodine consumed, except in the case of castor oil, when it amounts to 60—65%. R. B.

Autoxidation of Fats. G. R. Greenbank and G. E. Holm (*Ind. Eng. Chem.*, 1924, **16**, 598—601).—The presence of water and water vapour seems to retard the autoxidation of fats, and to a greater or less extent the formation of those compounds that are responsible for the tallowy odour. Fatty acids act probably indirectly as catalysts for autoxidation, through the liberation of unsaturated acids (especially oleic acid) which are strongly catalytic in this reaction. The resistance of butter fat to autoxidation may be increased by thorough washing of the fat or by passing steam through it, but prolonged heating or steam treatment has the opposite effect. The results of experiments at 95° on the rate of absorption of oxygen by butter fat in the dry condition and mixed with water, oleic acid, and butyric acid, respectively, are given graphically. The addition of water increases the period of induction before the absorption of oxygen begins. Once the absorption commences, the shape of the curves is almost identical whether fatty acid or water is present or not. The presence of free fatty acids decreases the period of induction, oleic acid being more effective in this respect than butyric acid. H. C. R.

I. Oxidation of Sodium Lactate by Hydrogen Peroxide. II. Effect of Cystine and Glycine on the Oxidation of Sodium Lactate by Hydrogen Peroxide. G. B. Ray (*J. Gen. Physiol.*, 1924, **6**, 509—523, 525—529).—I.—The reaction between hydrogen peroxide and sodium lactate was studied by observing the rate of production of carbon dioxide and by titrating the amount of peroxide present at various stages. In the early stages of the reaction there was found an increased amount of peroxide when the experiment was performed in the presence of air, but not in its absence. In the latter case, the end-product of the reaction was acetaldehyde. From these results and from the observations on the carbon dioxide production, the author concludes that the reaction is of an autocatalytic type and that the increased peroxide observed in the presence of air is due to the formation of acetyl peroxide from the acetaldehyde which is the first product of reaction. Ferric chloride increases the production of carbon dioxide if added to the peroxide solution first, but inhibits it if added first to the sodium lactate.

II.—The rate of production of carbon dioxide in the reaction above described is augmented considerably by the presence of cystine and slightly by glycine. Since it is influenced by the presence of the sulphydryl group, the process is probably one of dehydrogenation. C. R. H.

Aliphatic Hydroxy-acids. I. M. Asano (*J. Pharm. Soc. Japan*, 1924, No. 504, 75—86).—Heptoyl chloride was converted into ethyl heptoylacetoacetate from which the acetyl group was removed with ammonia and the product reduced with sodium amalgam to β-hydroxypelargonic acid, m. p. 59—60°. *Ethyl hydrogen azelate*, b. p. 169—170°/2 mm., 178°/4 mm., 193°/9 mm., m. p. 26—27°, was prepared by heating a mixture of azelaic acid (1 mol.) and anhydrous ethyl alcohol (2·5 mols.) or a mixture of ethyl azelate (1 mol.) and water (2·5 mols.) in a sealed tube at 150° during 6 hours. The yields in both the methods do not exceed 50%, but no resinous substance is produced. Ethyl hydrogen pimelate, b. p. 166°/5 mm., 155°/2 mm., is prepared by the same method. By the action of zinc propyl iodide on ethyl azelayl chloride, *ω-butyroyloctoic acid*, $C_3H_7\cdot CO\cdot[CH_2]_7\cdot CO_2H$, m. p. 56°, is produced; *semicarbazone*, m. p. 131°. A small amount of *αη-dibutyroylheptane*, $(C_3H_7\cdot CO)_2[CH_2]_7$, m. p. 71°, was produced as a by-product; the *disemicarbazone* melts at 166°. The conversion of the ketonic acid into its chloride did not proceed smoothly.

K. K.

Influence of the Base on the Degree of Conversion of Primary Salts of Dibasic Acids in Aqueous Solution. T. Sabalitschka and G. Kubisch (*Z. anorg. Chem.*, 1924, **134**, 79—86).—The authors have determined the acid content of ethereal extracts of aqueous solutions of the primary salts of camphoric, oxalic, succinic, fumaric, and maleic acids with potassium, sodium, lithium, ammonium, aniline, carbamide, and benzamide. For the primary camphorates, oxalates, succinates, and fumarates of potassium, sodium, lithium, and ammonium, similar amounts of free acid pass into the ethereal layer. In some cases, *e.g.*, in the case of benzamide oxalate and maleate, the ether dissolves some of the salt. The greater free acid content of the ether in the case of the primary salts of aniline, carbamide, and benzamide than in that of alkali and ammonium salts is conditioned by hydrolytic decomposition. The relation of acid transference, aniline salt < carbamide < benzamide, is for aniline and carbamide in agreement with the known dissociation constants. Camphoric and fumaric acids liberated from the primary alkali and ammonium salts pass completely into the ethereal layer, succinic acid less completely, and oxalic and maleic acids only very slightly. The conversion of the acid salt depends on the distribution of the free acid between ether and water and the ratio of the dissociation constant of both hydrogen atoms. The degree of conversion of the acid salt to normal salt and free acid in aqueous solution is for the individual salts of that acid the same so long as the salt undergoes no appreciable hydrolytic decomposition. The degree of decomposition is independent of the base so long as it is sufficiently strong to give salts which are not appreciably hydrolysed. J. B. F.

Syntheses using Sodamide. XII. Action of Ethyl Chloroformate on the Sodium Compounds of certain Ketones. A. Haller and E. Bauer (*Ann. Chim.*, 1924, [x], **1**, 275—297).—After treatment with sodamide, phenyl *iso*propyl ketone interacts with ethyl chloroformate to yield chiefly *α-phenyl*-β-*methyl*-Δ^α^-*propenyl ethyl carbonate*, $CMe_2{:}CPh\cdot O\cdot CO_2Et$, m. p. 41—42°, b. p. about 135°/10 mm.; the product is hydrolysed to the original ketone, gives no oxime, and generally is quite different from its isomeric *C*-derivative, ethyl α-benzoyl*iso*butyrate (Blaise and Courtot, A., 1906, i, 794). When the *oxime* of the latter (needles, m. p. 135—136°) is subjected to hydrolysis, or prepared directly in alkaline solution, it is converted into 3-phenyl-4 : 4-dimethyl*iso*oxazolone, m. p. 70—71°. The sodium compound of phenyl ethyl ketone and ethyl chloroformate produces two compounds, viz., *α-phenyl-Δ^{α}-propenyl ethyl carbonate*, b. p. 140—145°/11—12 mm., and the *ethyl carbonic* ester of *ethyl β-hydroxy-α-methylcinnamate*, $CO_2Et{\cdot}O{\cdot}CPh{:}CMe{\cdot}CO_2Et$, b. p. 182—185°/11 mm., which, on hydrolysis, affords ethyl α-benzoylpropionate (Perkin and Calman, T., 1886, **49**, 156); this interacts with hydroxylamine in alkaline solution to form 3-phenyl-4-methyl*iso*oxazolone, needles, m. p. 123—124°. From phenyl propyl ketone are similarly obtained *α-phenyl-Δ^{α}-butenyl ethyl carbonate*, b. p. 143°/10 mm., and the *ethyl carbonic* ester of *ethyl β-hydroxy-α-ethylcinnamate*, m. p. 35°, b. p. 183—184°/10 mm., which yields, when hydrolysed, *ethyl α-benzoylbutyrate*. The *oxime* of the latter forms scales or needles, m. p. 80—81°; Hantzsch and Miolati's product (A., 1893, i, 583), m. p. 90—91°, is 3-phenyl-4-ethyl*iso*oxazolone, not the simple oxime. Acetophenone, treated with sodamide followed by ethyl chloroformate, yields ethyl benzoylmalonate (Bernhard, A., 1895, i, 93), a *compound*, $C_{11}H_{14}O_4$, b. p. 128—129°/11 mm., and the ethyl carbonic ester of ethyl β-hydroxycinnamate (Bernhard, *loc. cit.*). Di*iso*propyl ketone similarly yields chiefly *ethyl βδ-dimethyl-Δ^{β}-pentenyl carbonate*,

$$CHMe_2{\cdot}C(O{\cdot}CO_2Et){:}CMe_2,$$

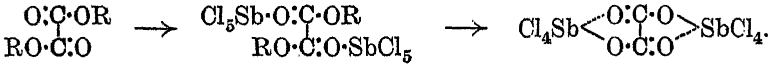
b. p. 86°/15 mm., whilst pentamethylacetone, from the above *iso*butyrone, sodamide, and methyl iodide, gives *ethyl βδδ-trimethyl-Δ^{β}-γ-pentenyl carbonate*, b. p. 104—107°/24—25 mm. *cyclo*Hexanone, by similar treatment, is converted into a mixture of Δ^1-cyclo*hexenyl ethyl carbonate*, b. p. 108—110°/20 mm., and bis*cyclo*hexenehexanone (Wallach, A., 1897, i, 160). W. A. S.

Bismuth Oxalates. E. Moles and R. Portillo (*Anal. Fis. Quim.*, 1924, **22**, 187—197; cf. this vol., i, 9).—According to the method of preparation, bismuth oxalate monohydrate is obtained with colours varying from brick-red to pink. The velocity with which water is absorbed on exposure in a moist atmosphere differs with the colour of the monohydrate. The red monohydrate absorbs water more quickly than the pink monohydrate, and when dried over sulphuric acid loses 3 of the 6 mols. of water thus absorbed, whilst in the case of the pink monohydrate 5 mols. of water are taken up, of which 3 are lost on drying over sulphuric acid. It is supposed that the single molecule of water in the monohydrate is more closely associated with the nucleus than the molecules which are absorbed from a moist atmosphere. Four hydrates are mentioned containing, respectively, 6, 5, 3, and 2 mols. of water in addition to the single molecule associated with the nucleus. G. W. R.

Thermal Decomposition of Calcium Oxalate. E. Moles and C. Díaz Villamil (*Anal. Fis. Quim.*, 1924, **22**, 174—186).—When traces of moisture are present, the initial temperature of decomposition of anhydrous calcium oxalate is 380°; carbon monoxide and carbon dioxide are evolved together with water vapour, and the residue of calcium carbonate is grey in colour and contains carbon and traces of formic acid. Using perfectly dry anhydrous calcium oxalate, the decomposition also begins at 380°, and is represented by the equation, $CaC_2O_4 \rightleftharpoons CaCO_3+CO$. The decomposition is thus incomplete and the residue contains calcium oxalate. At higher temperatures (470—480°), the decomposition is represented by the equation $7CaC_2O_4=7CaCO_3+5CO+CO_2+C$.

G. W. R.

Reaction between Antimony Pentachloride and Ethyl Oxalate. P. Pfeiffer (*Z. anorg. Chem.*, 1924, **133**, 101—106).—The behaviour of antimony pentachloride towards *o*-hydroxy-ketones is exactly analogous to that of stannic chloride (A., 1913, i, 879). Two mols. of the ketone combine with 1 mol. of the halide and, on warming, 1 mol. of ketone and 1 mol. of hydrogen chloride are eliminated. Thus β-acetyl-α-naphthol reacts to give β-*acetyl-α-naphthoxy-antimony tetrachloride*, $Ac\cdot C_{10}H_6\cdot O\cdot SbCl_4$. Ethyl oxalate behaves similarly (cf. A., 1902, i, 358):



$$\begin{array}{l}O{:}C\cdot OR\\ RO\cdot C{:}O\end{array} \longrightarrow \begin{array}{l}Cl_5Sb\cdot O{:}C\cdot OR\\ \quad RO\cdot C{:}O\cdot SbCl_5\end{array} \longrightarrow Cl_4Sb{<}\begin{array}{l}O{:}C\cdot O\\ O\cdot C{:}O\end{array}{>}SbCl_4.$$

S. K. T.

Stereoisomerism and Steric Transformations among α-Thio- and α-Sulpho-di[alkyl]carboxylic Acids. R. Ahlberg (*J. pr. Chem.*, 1924, [ii], **107**, 241—329; cf. Lovén and Ahlberg, A., 1921, i, 223; Loven, A., 1908, i, 714, and earlier papers).—Sodium α-bromobutyrate and sodium sulphide interact in aqueous solution to give almost equimolecular proportions of *meso*-α-thiodibutyric acid, $S(CHEt\cdot CO_2H)_2$, m. p. 109° (Lovén, *loc. cit.*), and the *racemic* isomeride, m. p. 82°. The *potassium hydrogen* salt is described. The acid is resolved with the help of the active phenylethylamines. l-*Phenylethylammonium* l-*thiodibutyrate*, m. p. 142—143°, $[\alpha]_D$ −46·0°, and d-*phenylethylammonium* d-*thiodibutyrate*, $[\alpha]_D$ +43·6°, are described. l-α-*Thiodibutyric acid* forms prisms, m. p. 35°, $[\alpha]_D$ −152°; the *d*-variety has $[\alpha]_D$ +145°. Slow racemisation takes place in aqueous solution at 100°. The normal *silver, potassium hydrogen,* and d-*phenylethylammonium hydrogen* meso-α-*thiodibutyrates* were prepared. In preparing the α-thiodi*iso*valeric acid, it was found better to treat ethyl α-bromo*iso*valerate with alcoholic sodium sulphide; the crude *ethyl α-thiodi*iso*valerate* obtained had b. p. 165—168°/17 mm. It was hydrolysed and converted into the strychnine salt, which, fractionally crystallised, gave *meso*-α-thiodi*iso*valeric acid, m. p. 136° (cf. Lovén, *loc. cit.*), and small quantities of the *racemic* variety. The latter is also obtained by heating the *meso*-form at 200—210°, and in considerable proportion when the *diethyl* ester (b. p. 160—162°/13 mm.) of the latter is hydrolysed. The *potassium, sodium, magnesium, barium, calcium, strontium, copper, silver, strychnine, brucine,* and l-α-*phenylethylammonium* salts of *meso*-α-thiodi*iso*valeric acid were prepared.

The *ethyl* ester has b. p. 160—162°/13 mm. The *potassium hydrogen, potassium sodium, magnesium, barium, copper*, and *silver* salts of the *r*-acid are described. The acid is resolved into optically active components by means of *l*-phenylethylamine or brucine. d-α-*Thiodi*iso*valeric acid* has m. p. 80·5—81°, $[\alpha]_D$ +129°; the *lævo isomeride* has m. p. 81—81·5° and $[\alpha]_D$ −126·5°. The brucine salts were isolated. The solubilities of all these acids and of many of their salts are recorded, and also the affinity constants, from conductivity measurements, for the acids. It is shown that, for the series α-thiodiacetic acid–α-thiodi*iso*valeric acid, the racemic form in every case is the stronger acid, whilst the optical activity (for the three acids possessing the property) decreases with rise in molecular weight for the acids, but increases for their salts. *meso*-α-Thiodibutyric acid oxidised with alkaline permanganate yields the sulphone, *r*-α-sulphodibutyric acid (Lovén, *loc. cit.*); *l*-α-thiodibutyric acid similarly oxidised gives a lævorotatory product which, even in cold aqueous solution, rapidly loses its optical activity and the same product as from the inactive thio acid can be isolated. Optically active acids were, nevertheless, isolated from the brucine salts of the racemic sulphone acid, but rapid racemisation prevented their characterisation in any other way than by the optical activity of the solutions; d-α-*sulphodibutyric acid* crystallises but has no definite m. p. The *potassium hydrogen* salt of the meso variety is described. *r*-α-Thiodi*iso*valeric acid carefully oxidised with alkaline permanganate gives r-α-*sulphoxydi*iso*valeric* acid, m. p. 152—152·5°. The *meso*-thio acid, further oxidised, yields a little of this, together with a mixture of *racemic* (Lovén, *loc. cit.*) and meso-α-*sulphodi*iso*valeric acids*, m. p. 131—133°; the *sodium, potassium, magnesium, zinc, calcium, barium, cinchonine, brucine*, and *strychnine* salts are described. The *potassium hydrogen* and *barium* salts of the corresponding *r*-acid were prepared. Oxidation of the optically active α-thiodi*iso*valeric acids yields optically active products which rapidly racemise, but they can be isolated by fractionally crystallising the brucine and cinchonine salts of the racemic variety. The brucine salt of l-α-*sulphodi*iso*valeric* acid has m. p. 139° and the free acid $[\alpha]_D$ −30·6°; the cinchonine salt of the *d*-variety (decomp. 115°) similarly gives an acid, $[\alpha]_D$ +30·2°. Both rapidly racemise in warm aqueous solution. The author discusses at length the mechanism of the racemisation and the conversion of the meso into the racemic forms. The reactions are unimolecular and evidently depend on enolisation, either through the carboxy or the sulpho group, or both. W. A. S.

"Alcoholic Fermentation" of Formaldehyde by Osmium. II. E. Müller (*Z. physikal. Chem.*, 1923, **107**, 347—356; cf. A., 1922, i, 110).—Osmium catalyses the reduction of formaldehyde to methyl alcohol only when present in the colloidal or highly dispersed condition. The metal is obtained in this condition by adding to the formaldehyde an osmium compound, such as osmic acid, which is then reduced to the metal in a highly active form. An examination of the catalytic reaction at 100° shows that the gas evolved is not entirely carbon dioxide as the equation $3H{\cdot}CHO+H_2O=CO_2+2CH_3{\cdot}OH$ demands, but contains hydrogen and methane in addition, and sometimes, although in very small quantities, carbon monoxide. The formation of hydrogen and methane is due to the changes, $H{\cdot}CHO+H_2O=2H_2+CO_2$ and $2H{\cdot}CHO=CH_4+CO_2$. Experiments show that an increasing evolution of methane is accompanied by a decreasing evolution of hydrogen and that as the ratio, volume of aldehyde solution: weight of osmium, increases the amount of methane formed decreases, the reaction producing the alcohol always predominating. The time taken for the catalytic action and the gas evolution to reach a maximum is increased by increasing p_H, and the magnitude of the maximum is reduced. The induction period before the catalytic action begins appears to be the same whether the formaldehyde is heated with the osmium compound or kept cold, and the catalysis differs little whether the osmium is added in the form of the tetroxide, potassium osmate, or potassium chloro-osmate. The volume relations of the gases evolved are about the same in all cases, and when the reaction is concluded the osmium is present in the colloidal condition. The similarity between the present reaction and fermentation by yeast is pointed out. J. F. S.

Formaldehyde. H. VON WARTENBERG, A. MUCHLINSKI, and G. RIEDLER (*Z. angew. Chem.*, 1924, **37**, 457—459).—The heat of combustion of formaldehyde and its polymerides has been redetermined as follows: $CH_2O_{gas}+O_2=CO_2+H_2O_{liq.}+15{\cdot}88\pm0{\cdot}033$ Cal.; $CH_2O_{para}+O_2=CO_2+H_2O_{liq.}+12{\cdot}21\pm0{\cdot}0085$ Cal.; $\frac{1}{3}(CH_2O)_3+O_2=CO_2+H_2O_{liq.}+10{\cdot}95\pm0{\cdot}007$ Cal. From this it follows that the heat of transformation of formaldehyde into paraformaldehyde and α-trioxymethylene is as follows: $CH_2O_{gas} \longrightarrow CH_2O_{para}+36{\cdot}7$ Cal. $\longrightarrow \frac{1}{3}(CH_2O)_3+1{\cdot}26$ Cal. and the heat of formation of gaseous formaldehyde from its elements is $C_{diamond}+\frac{1}{2}O_2+H_2=CH_2O_{gas}+4{\cdot}0\pm0{\cdot}3$ Cal. Attempts to synthesise formaldehyde by subjecting mixtures of carbon monoxide and hydrogen to the silent electric discharge at pressures up to 30 atms. gave only the merest trace of the substance. A mixture of carbonyl chloride with 15 times its volume of hydrogen yielded 3·6% of the theoretical amount of formaldehyde when passed over nickelised pumice at 300°. A maximum yield of 2% of formaldehyde based on the methane content of a mixture of methane and ozone was obtained when the mixture was passed over silver or lead chromate at 650°; at higher temperatures the yield rapidly fell to zero. A. R. P.

Rate of Oxidation of Aldehydes. M. SEIJOO (*Anal. Asoc. Quím. Argentina*, 1923, **11**, 151—171).—Data are given for the velocity of oxidation of formaldehyde, acetaldehyde, and benzaldehyde, respectively, by potassium permanganate and sulphuric acid. The reaction is found to be unimolecular when very dilute solutions of potassium permanganate are used. G. W. R.

Tautomerism of Ethyl Acetoacetate and Acetylacetone. Absorption Spectra of These and Related Compounds. P. GROSSMANN (*Z. physikal. Chem.*, 1924, **109**, 305—352).—The proportion present of the enolic form of ethyl acetoacetate and acetylacetone in various solvents, both pure and mixed in varying proportions, has been determined by titration with bromine and by quantitative absorption spectra measurements. The proportion found may vary slightly with concentration even for very dilute solutions, but no explanation of this is suggested. The velocity of the isomeric change was studied in various solvents, but in spite of careful purification, the reaction proved too susceptible to catalytic influence for reproducible results. In several cases, determinations were made at 0° and 25° and the heats of reaction calculated, but these varied with the solvent. Alkaline solutions were studied by a slight modification of the usual practice. Instead of acidifying the solution before treating with bromine, with consequent ketisation, acid bromine solution was added direct and excess bromine removed by aniline hydrochloride. Results were confirmed by spectroscopic measurements. Excess of alkali favours the enolic form. Similar results were obtained with acetylacetone. With still greater excess of alkali, the results are even higher, corresponding with the presence of a dienol. Analogous results are afforded by acetylacetone.

On warming alkaline solutions of ethyl acetoacetate, ketonic fission takes place, but, in the cold, hydrolysis occurs slowly and quantitatively. The course of hydrolysis was followed simultaneously with the proportion present of the enolic form. The resulting solution of sodium acetoacetate is only 0·2% enolic if the ester and alkali are mixed in equivalent proportions, but with excess alkali this is increased and, in great excess of alkali, may attain 5%. In spite of the complication of formation of enol, the reaction is bimolecular. Acetylacetone hydrolyses to acetone and sodium acetate quantitatively: the reaction corresponds with the simultaneous hydrolysis of the ketonic and enolic (and perhaps the dienolic) forms at different rates. In both cases, the conductivity scarcely alters during hydrolysis, so the enolic forms must be ionised about as highly as sodium acetate, and complex formation is excluded.

The ultra-violet absorption spectra of ethyl acetoacetate and acetylacetone and other substances of similar composition in various solvents are given quantitatively. That of ethyl acetoacetate in the vapour state at room temperature was also studied and found closely to resemble that of the pure liquid. It is deduced that 5% must be in the enolic form. A ring structure in the gaseous state is excluded, as the band is continuous and cannot be resolved into the fine lines characteristic of unsaturated ring compounds.

L. J. H.

Keto-enolic Desmotropy. III. Determination of Enols by Titration with Thiocyanogen. H. P. Kaufmann and G. Wolff (*Ber.*, 1924, 57, [*B*], 934—937).—Experiments with ethyl acetoacetate, acetyldibenzoylmethane, ethyl diacetylsuccinate, and ethyl formylphenylacetate show that the equilibrium of keto-enolic desmotropes can be determined by titration with thiocyanogen if the rate of transformation is sufficiently slow; nitromethane is particularly suitable as a solvent. From the points of view of convenience and general applicability, the method is inferior to Meyer's bromine titration method. H. W.

Compounds of Quadrivalent Nickel with Dimethylglyoxime. F. Feigl.—(See ii, 504.)

Colour Reaction between Cobalt Salts and Dimethylglyoxime in the Presence of Sulphides. F. Feigl and L. von Tustanowska.—(See ii, 504.)

Oxidation of Carbohydrates with Air. H. A. Spoehr (*J. Amer. Chem. Soc.*, 1924, **46**, 1494—1502).—Methylene-blue is reduced by dextrose in solutions containing disodium phosphate, the rate of reduction being proportional to the concentration of the latter from 0·025 to 0·75*M*, and to that of the dextrose from 0·05 to 0·5*M*. On drawing a stream of air through the solution, the blue colour is restored and carbon dioxide formed. Lævulose reacts similarly, from five to eight times as rapidly as dextrose. The rate of production of carbon dioxide is increased threefold by the addition of a trace of a solution of ferric phosphate in sodium citrate ("soluble ferric phosphate"). The methylene-blue is gradually consumed, possibly on account of production of hydrogen peroxide. Sodium ferropyrophosphate, $Na_8Fe_2(P_2O_7)_3$, catalyses the above reaction, and also brings about atmospheric oxidation of dextrose alone, the rate of formation of carbon dioxide first increasing rapidly and then slowly diminishing. Sodium ferripyrophosphate, $Na_6Fe_2(P_2O_7)_3$, is less active, and sodium manganopyrophosphate shows only about 0·1% of the activity of iron. Prior aëration of the catalyst has no effect on its activity. Maximum oxidation was attained at p_H 7·2. *d*-Mannose, *d*-galactose, sucrose, trehalose, and mannitol are also oxidised in presence of sodium ferropyrophosphate, disodium phosphate, and potassium dihydrogen phosphate, the oxidation of sucrose also proceeding in solution of p_H 6·8. Evidence of hydrolysis of sucrose and trehalose prior to oxidation was not obtained. The oxidation of dextrose is probably accompanied by partial conversion into lævulose and ketoses, and some formation of saccharic acid. F. G. W.

Behaviour of Sugars in Dilute Alkaline Solutions. I. Cause of the Transformation of Dextrose in Dilute Solutions of Potassium Hydroxide. J. Groot (*Biochem. Z.*, 1924, **146**, 72—90).—The lowering of rotation of dextrose solutions of various concentrations from 0·16*M* to 0·66*M*, in the presence of potassium hydroxide varying between 0·05*N* and 1·0*N* has been studied quantitatively. For various concentrations of dextrose the extent to which the rotation is lowered increases with increasing hydroxide concentration, the limiting value being about 2/9 of the rotation of the original dextrose solution at equivalent dilution. For any given concentration of dextrose the velocity of the decrease in rotation increases with increasing hydroxide concentration, until a limiting value is reached beyond which further increases in the hydroxide concentration produce no effect on the velocity of the change of rotation. The latter attains its maximum when the ratio of dextrose to potassium hydroxide is unimolecular, and this is independent of the original dextrose concentration. The results resemble the de Bruyn–van Ekenstein transformation and are interpreted as representing the conversion of dextrose into a mixture of this and other hexoses which proceeds as a unimolecular reaction, the following equation being deduced as applying within the limits between which K varies with N: $K=12{\cdot}8M/N$ (at 25°), where K=velocity constant with a maximum value of 12·8, M=molar concentration of dextrose, and N=normality of the potassium hydroxide. In a theoretical discussion of the results the view is expressed that the cause of the changes observed is the formation of potassium glucosate, $C_6H_{11}O_6K$, and the instability of this compound in aqueous solution. J. P.

Fluoro-acetyl Derivatives of Sugars. III. Optical Rotation and Atomic Dimension. D. H. Brauns (*J. Amer. Chem. Soc.*, 1924, **46**, 1484—1488).—*Fluorotriacetyl*-l-*arabinose* forms brilliant needles, m. p. 117—118°, $[\alpha]_D^{20}$ +138·18° in chloroform. Chlorotriacetyl-*l*-arabinose has $[\alpha]_D^{20}$ +244·32° (cf. Chavanne, A., 1902, i, 346; Ryan and Mills, T., 1901, **79**, 706), and bromotriacetyl-*l*-arabinose has m. p. 138—139°, $[\alpha]_D^{20}$ +287·11° (cf. Chavanne, *loc. cit.*). *Iodotriacetyl*-l-*arabinose*, prepared similarly to iodo-tetra-acetylglucose (E. and H. Fischer, A., 1910, i, 716), forms colourless crystals, $[\alpha]_D^{20}$ +339·06°. The differences in specific rotations of the above compounds are approximately proportional to the differences in atomic diameters of the halogen atoms, and are in agreement with similar relationships previously found for analogous derivatives of other carbohydrates. F. G. W.

Halogen Compounds of Starch. M. Bergmann and S. Ludewig (*Ber.*, 1924, **57**, [*B*], 961—963).—Starch acetates, obtained by short treatment of starch with a saturated solution of hydrogen chloride in acetic anhydride at 0°, retain the typical affinity of starch towards mixtures of iodine and potassium iodide and the power of absorbing bromine, thus lending support to the authors' view (this vol., i, 618) that the formation of halogen compounds is attributable to certain bridge oxygen atoms of starch. H. W.

Alkoxyl Groups of the Wood and Lignin of the Pine. E. Hägglund and B. Sundroos (*Biochem. Z.*, 1924, **146**, 221—225).—From determinations of the alkoxyl content of pine wood and of the lignins prepared from it, by the Zeisel and Feist-Willstätter methods, and since the latter method yields only phenyltrimethylammonium iodide or tetramethylammonium iodide, it is concluded that the alkoxyl groups consist wholly of methoxyl. J. P.

Ammonia and Amine Compounds of Stannic Dialkyl Halides. P. Pfeiffer (*Z. anorg. Chem.*, 1924, **133**, 91—100).—Stannic dialkyl halides combine with quinoline or aniline to give crystalline additive compounds which are unstable towards heat and have indefinite melting points (cf. A., 1911, i, 747). Dry ammonia combines with stannic dialkyl halides at the ordinary temperature to form additive ammonia compounds in which the co-ordination number of the tin is probably 8 (cf. A., 1923, ii, 867).

Diquinoline stannic dimethyl chloride, $SnMe_2Cl_2,2C_9H_7N$, forms white crystals, m. p. 40—60°, unstable in moist air; the corresponding *bromide*, m. p. 80—115°, behaves similarly. *Dianiline stannic dimethyl chloride*, $SnMe_2Cl_2,2PhNH_2$, when dissolved in pyridine, yields the corresponding pyridine compound; the *iodide* forms unstable, pale yellow crystals. *Dianiline stannic diethyl chloride* and the *bromide*, $SnEt_2X_2,2PhNH_2$, *monoaniline stannic diethyl bromide* and *dianiline stannic dipropyl bromide* were also prepared.

The *ammonia* compounds, $SnR_2X_2,4NH_3$, were prepared, where R=Me, X=Cl, Br and I; R=Et, X=Br and I; R=Pr, X=Cl and Br. The compound with R=Et and X=Cl contained only $3NH_3$. S. K. T.

Organic Silver Complexes. F. G. Pawelka (*Z. Elektrochem.*, 1924, **30**, 180—186).—By the use of the method described by Bödlander, the complexity of a number of additive derivatives of organic substances and silver nitrate has been determined. If the complexes are considered to be of the general type, $[Ag_mR_n](NO_3)_m$, then $m=1$ and $n/m=2$ in the case of the following silver derivatives: sodium thiosulphate, dimethylamine, diethylamine, triethylamine, hexamethylenetetramine, glycine, acetonitrile, propionitrile, ethylene cyanide, and toluidine. In the case of thiocarbamide, $m=1$ and $n/m=3$. H. T.

Preparation of *p*-Aminobenzoyl Derivatives of δ-Methyl-β-dimethyl(diethyl)aminopentan-α-ol. Chemische Fabrik Flora (Brit. Pat. 200810).—δ-Methyl-β-dimethyl(diethyl)aminopentan-α-ol (cf. Karrer and others, this vol., i, 168) is converted into the *p*-nitrobenzoic ester and the latter is reduced. δ-*Methyl*-β-*diethylaminoamyl* p-*nitrobenzoate hydrochloride*, m. p. 163°, and δ-*methyl*-β-*diethylaminoamyl* p-*aminobenzoate hydrochloride*, m. p. 190°, are described. The latter substance has valuable therapeutic properties. W. T. K. B.

Mixed Crystals, consisting of 2 Mols. of Glycine, or 2 Mols. of Alanine, or 1 Mol. of Glycine and 1 Mol. of Alanine, combined with 1 Mol. of Hydrochloric Acid. E. Abderhalden and H. Sickel (*Z. physiol. Chem.*, 1924, **135**, 29—31).—From the strongly acidified mother-liquors of a tyrosine preparation the authors isolated crystals of *glycinealanine monohydrochloride*, rectangular needles, m. p. 177° after softening at 105°, $[\alpha]_D^{19}$ +4·42°. Recrystallisation from water gave rhombic crystals of *diglycine monohydrochloride*, m. p. 178°. The crystals, together with *dialanine monohydrochloride*, m. p. 214°, $[\alpha]_D^{21}$ +9·13°, were also prepared directly from the amino-acids and hydrochloric acid by slow evaporation. E. M. C.

Action of Sulphuric Acid on some Amino-acids and on the Vinasse from the Distillation of Molasses. P. G. Kronacker (*Bull. Soc. chim. Belg.*, 1924, **33**, 217—231).—Determinations have been made of the proportions of nitrogen convertible into ammonium sulphate by the action of sulphuric acid on various amino-acids known to be present in sugar juices. The whole of the nitrogen in glycine, asparagine, aspartic acid, glutamic acid, and leucine was converted by treatment with sulphuric acid (66%). In the case of betaine it was necessary to use 95% acid with permanganate or mercury. It is suggested that dehydration causes betaine to form a stable ring compound. On treatment with 66% acid, tryptophan gave a low result which is ascribed to the formation of a stable tautomeric form; the theoretical value was obtained when the Stolzenberg–Kjeldahl method was used. Arginine gave a low result when treated with 66% acid. F. B.

Sulphamic Ester and its Isomerisation to Compounds of the Betaine Type. W. TRAUBE, H. ZANDER, and H. GAFFRON (*Ber.*, 1924, 57, [*B*], 1045—1051).—An attempt to prepare methyl sulphamate by the action of diazomethane on the acid led to the production of a *substance*, m. p. 239°, which is also obtained, in 93% yield, by the action of methyl iodide on dry silver sulphamate at the ordinary temperature. On account of its difference in properties from the dimethylsulphamic esters prepared by Behrend (A., 1884, 285), the constitution, $\overline{NMe_3\cdot SO_2\cdot O}$, is ascribed to the substance, which is thus *anhydrotrimethylsulphamic acid*. The isomeric *methyl dimethylsulphamate*, pale or yellow oil, obtained by the action of sodium methoxide on dimethylsulphamyl chloride, undergoes conversion into the trimethylsulphamic acid even at the ordinary temperature, and is probably produced intermediately in the formation of trimethylsulphamic acid. The reaction with silver sulphamate proceeds according to the equation $3NH_2\cdot SO_3Ag+3MeI=\overline{NMe_3\cdot SO_2\cdot O}+2NH_2\cdot SO_3H+3AgI$, two-thirds of the silver sulphamate being found as free sulphamic acid. The course of this reaction depends on the weight of the alkyl radical participating. Thus with ethyl iodide the product is *ethyl diethylsulphamate*, $NEt_2\cdot SO_3Et$, in 80% of the theoretical yield, whilst with benzyl chloride in chloroform solution the product is *benzyl benzylsulphamate*, m. p. 90°. R. B.

Determination of the Constitution of the Eutectic Mixture of Methyl, Ethyl, and *iso*Butyl Oxamates. A. PRAETORIUS (*Z. anal. Chem.*, 1924, 64, 96—102).—By thermal analysis, the results of which are plotted on a triangular diagram, the eutectic mixture, m. p. 56°, of methyl, ethyl, and *iso*butyl oxamates was found to consist of 16·5% of the methyl, 24·5% of the ethyl, and 59% of the *iso*butyl ester. The error in calculating the result from the analytical figures for carbon and nitrogen amounted to 10%. A. R. P.

Chlorides of Thiocyanogen. H. P. KAUFMANN and J. LIEPE (*Ber.*, 1924, 57, [*B*], 923—928).—Thiocyanogen dissolved in cold chloroform reacts with chlorine in three ways, yielding, respectively, *thiocyanogen monochloride*, (SCN)Cl, sulphur chloride and cyanuric chloride, and *thiocyanogen trichloride*, $(SCN)Cl_3$. The monochloride crystallises in colourless needles which become yellow at about 150° and darken, without melting, at a higher temperature. It is comparatively stable towards water, by which it is ultimately hydrolysed to sulphur, hydrocyanic, hydrochloric, thiocyanic, and sulphuric acids. The trichloride, which is more conveniently prepared in ethyl bromide solution, is a yellow liquid with a very unpleasant odour, b. p. 54—56°/20 mm., 152—153°/760 mm. It is slowly decomposed by cold water into sulphur, thiocyanic, hydrocyanic, hydrochloric, and sulphuric acids and by sodium hydroxide solution (10%) into hydrocyanic, thiocyanic, hydrochloric, sulphurous, thiosulphuric, and sulphuric acids, hydrogen sulphide, carbon dioxide, and ammonia. H. W.

Titrations with Free Thiocyanogen. H. P. KAUFMANN and P. GAERTNER (*Ber.*, 1924, **57**, [*B*], 928—934).—Solutions of thiocyanogen in organic media can be accurately titrated by agitation with at least twice the equivalent quantity of potassium iodide dissolved in water and determination of the liberated iodine. In cases in which the end-point is obscured by the separation of thiocyano compounds, alcoholic sodium iodide solution may replace aqueous potassium iodide. The application of thiocyanogen in volumetric analysis is restricted by the necessity of using anhydrous solvents and dry vessels to avoid hydrolysis, and by the limited stability of such solutions owing to the tendency towards polymerisation. With a sufficient excess of sodium thiosulphate or hydrogen sulphide, respectively, thiocyanogen reacts quantitatively according to the equations $2Na_2S_2O_3+(CNS)_2=2NaSCN+Na_2S_4O_6$ and $(SCN)_2+S''=2SCN'+S$. In carbon tetrachloride solution, antipyrine reacts rapidly and quantitatively with an excess of thiocyanogen, whereas α- and β-naphthols react similarly, but more slowly. Thymol dissolved in nitromethane is moderately rapidly transformed into 4-*thiocyano*-6-iso*propyl*-m-*cresol*, yellow needles, m. p. 108—109°. H. W.

Thiocyanatocobaltous Acid and its Alkali Salts. F. J. ALLEN and A. R. MIDDLETON (*Proc. Indiana Acad. Sci.*, 1922, 153—158).—Experiments on the partition of sulphuric acid, thiocyanic acid, and cobalt between water and a 1 : 4-mixture of ethyl alcohol and ethyl ether showed the ether layer to contain equivalent proportions of cobalt and thiocyanate, and larger amounts of thiocyanic acid, but practically no cobalt thiocyanate or potassium thiocyanate; they do not elucidate the composition of the blue compounds obtained by Rosenheim and Cohn (A., 1901, i, 455), which probably consist of one or more complex acids, $H_{2x}Co(SCN)_{4x}$, containing cobalt in the anion. Both the blue complex alkali thiocyanatocobaltites and the purple compound, $Co(SCN)_2,3H_2O$, can be prepared by double decomposition in aqueous solution from cobalt sulphate, the alkali sulphate being removed with ethyl alcohol, thus avoiding the use of unstable thiocyanic acid. The form of the compounds, $K_2Co(SCN)_4$ and $(NH_4)_2Co(SCN)_4$ stable in air is the trihydrate (cf. Treadwell, A., 1901, ii, 284). The purple salt, $Co(SCN)_2,3H_2O$, on exposure to warm air, yields the yellowish-brown hemihydrate. CHEMICAL ABSTRACTS.

Double Salt of Zinc and Cæsium Ferricyanides. I. M. Kolthoff and E. J. A. H. Verzijl (*Rec. trav. chim.*, 1924, **43**, 394—396).—In the potentiometric titration of a zinc salt with potassium ferrocyanide containing a little ferricyanide, addition of cæsium chloride causes a considerable fall in the potential of the electrode (cf. this vol., ii, 501). This is due to the formation of a very sparingly soluble *zinc cæsium ferricyanide*,

$$2Zn_3[Fe(CN)_6]_2,Cs_3Fe(CN)_6,$$

the precipitation of which increases the ratio ferrocyanide : ferricyanide on which the electrode potential depends. E. H. R.

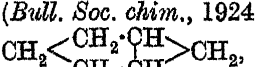
Addition of Mono- and Poly-hydric Alcohols and Mercaptans to Azodicarboxylic Ester. O. Diels and C. Wulff (*Annalen*, 1924, **437**, 309—318; cf. A., 1922, i, 774, 1194; 1923, i, 391; this vol., i, 673).—Azodicarboxylic ester reacts with alcohols and mercaptans with varying velocity, yielding additive compounds of 1 mol. of alcohol with 1 mol. of ester (2 mols. of ester in the case of glycols). In the presence of potassium acetate the additive compounds are decomposed, yielding nitrogen, hydrazo ester, and the alkyl carbonate. Methyl alcohol and methylazodicarboxylate yield the colourless *additive* compound,

$$CO_2Me\cdot N(OMe)\cdot NH\cdot CO_2Me,$$

a colourless, viscous oil, d_4^{20} 1·3024; $n_{H\alpha}^{20}$ 1·44475, n_D^{20} 1·44887. Similarly, ethyl alcohol and methyl azodicarboxylate yield the *compound*, $CO_2Me\cdot N(OEt)\cdot NH\cdot CO_2Me$, a bright, viscous, highly refracting oil, decomposing on distillation into nitrogen, hydrazo ester, and methyl ethyl carbonate. *iso*Butyl alcohol in 4—6 weeks yields the *compound*, $C_8H_{16}O_5N_2$, and amyl alcohol in 8 weeks the compound, $C_9H_{18}O_5N_2$, colourless, viscous, highly refracting oils. With ethyl mercaptan, methyl azodicarboxylate yields in 24 hours the *compound*, $C_6H_{12}O_4N_2S$, a thick, colourless oil, d_4^{20} 1·2537, $n_{H\alpha}^{20}$ 1·48330, $n_{H\beta}^{20}$ 1·49410, which with fuming hydrochloric acid is decomposed into nitrogen, methyl hydrazodicarboxylate, and ethyl disulphide. Ethylene glycol and methyl azodicarboxylate in cold ethereal solution in the presence of a little potassium acetate yield in 2—3 days a little dimethyl ethylene dicarbonate, and the *additive* compound, $C_{10}H_{18}O_{10}N_4$, d_4^{20} 1·3296, $n_{H\alpha}^{20}$ 1·44918, $n_{H\beta}^{20}$ 1·45734, which dissociates in acetone yielding ethylene carbonate and hydrazo ester, whilst with potassium acetate reaction takes place, yielding nitrogen, methyl hydrazodicarboxylate, and *dimethyl ethylene dicarbonate*, $(CH_2\cdot O\cdot CO_2Me)_2$, ester-like oil, b. p. 215—220°/760 mm., which on boiling in ether yields ethylene and dimethyl carbonates. R. B.

Catalytic Decomposition of Hexahydro-aromatic and Saturated Aliphatic Hydrocarbons. The Cracking of Petroleum. V. Grignard and R. Stratford (*Compt. rend.*, 1924, **178**, 2149—2152).—The effect of aluminium chloride as a catalyst in the cracking of hydrocarbons was studied at temperatures between 120° and 150°, the proportion of catalyst used being 20—30%. *cyclo*Hexane and methyl*cyclo*hexane remained unchanged, whilst *o*-dimethyl- and, less readily, *p*-dimethyl-*cyclo* hexane were transformed into the *m*-compound. With derivatives having a side-chain of 2 or 3 carbon atoms, branched or not, about 1—5% was cracked, giving a saturated aliphatic hydrocarbon and polymerised *cyclo*hexene, the remainder forming polymethyl*cyclo*hexanes with the methyl groups in the meta positions to each other. *m*-Diethyl*cyclo*hexane was chiefly converted into tetramethyl*cyclo*hexane with some butane. The three butyl*cyclo*hexanes were cracked to the extent of 13—15%, the normal and secondary compounds producing *n*-butane, the tertiary, a mixture of butanes. The uncracked portion gave tetramethyl*cyclo*hexanes. Amyl- and *iso*amyl-*cyclo*hexanes decompose to the extent of 70% and 42%, respectively, into methyl*cyclo*hexane and butane, the rest isomerising to tetra- and penta-methyl*cyclo*hexanes. *n*-Octane, βζ-dimethylhexane, *n*-decane, βη-dimethyloctane, and heptadecane all gave *n*-butane, the longer chains being broken at both ends simultaneously. A. COUSEN.

0 : 1 : 3-*dicyclo*Hexane. N. ZELINSKY and M. OUCHAKOFF (*Bull. Soc. chim.*, 1924, [iv], **35**, 484—487).—0 : 1 : 3-*dicyclo*Hexane,



$CH_2<\begin{matrix}CH_2\cdot CH\\ \vert\\ CH_2\cdot CH\end{matrix}>CH_2$, the simplest example of a combined three- and five-membered ring, is prepared by reduction, with sodium and alcohol, of ethyl 2-keto*cyclo*pentanecarboxylate to the corresponding glycol. The dibromide is formed by heating the latter under pressure with phosphorus tribromide at 100°, and by treatment with zinc powder gives dicyclo*hexane*, b. p. 78—79·5°/745 mm. It is not affected by bromine. A. B. H.

X-Ray Diffraction Patterns from Crystalline and Liquid Benzene. E. D. EASTMAN.—(See ii, 448.)

Sulphonation of *m*-Dinitrobenzene. R. H. GRIFFITH (*J. Chem. Soc.*, 1924, **125**, 1401—1402).—The direct sulphonation of *m*-dinitrobenzene with fuming sulphuric acid (18% SO_3) at 150—160° in the presence of mercury yields 3 : 5-dinitrobenzenesulphonic acid (A., 1903, i, 407) in 38% of the theoretical yield. The product is sensitive to alkali, and apparently changes readily to a nitrohydroxybenzenesulphonic acid. R. B.

***s*-Tribromobenzyl Chloride and some of its Transformations.** M. HENRAUT (*Bull. Soc. chim. Belg.*, 1924, **33**, 132—138).—Addition of benzyl chloride and bromine to anhydrous aluminium bromide yields 2 : 4 : 6-*tribromobenzyl chloride*, yellow crystals, m. p. 153—154°, which when oxidised by nitric acid under pressure is converted into 2 : 4 : 6-tribromobenzoic acid. The chloride reacts with potassium cyanide to form 2 : 4 : 6-*tribromophenylacetonitrile*, a brown solid, m. p. 138—139°, which on hydrolysis at 150° with alcoholic potassium hydroxide affords 2 : 4 : 6-*tribromophenylacetic acid*, m. p. 157—158°, of which the *chloride* and the *amide*, m. p. 162—163°, were prepared. H. J. E.

Polarity Effects in Aromatic Halogen Compounds. J. B. SHOESMITH, A. C. HETHERINGTON, and R. H. SLATER (*J. Chem. Soc.*, 1924, **125**, 1312—1319).—The hydrolysis of the isomeric ω-bromotoluic acids in alcohol is in accordance with the principle of induced alternate polarities (T., 1922, **121**, 1392; 1923, **123**, 2828), the meta-isomeride being more readily hydrolysed than the para-, whilst with hydrogen iodide the para- is more readily reduced than the meta-isomeride. The behaviour of the ortho-compound is abnormal in both cases, owing to phthalide formation due to spatial influences. Since benzyl bromide is more readily hydrolysed than any of the ω-bromotoluic acids, the introduction of the carboxyl group has stabilised the molecule as a whole. The hydrolysis of the nitrobenzyl bromides follows the same rule, the *m*-isomeride being the most readily hydrolysed, but the introduction of the nitro group into a very reactive molecule such as *p*-methoxybenzyl bromide diminishes the reactivity of the latter to the order of that of the unsubstituted compound. 3-Nitro-4-hydroxybenzyl bromide is more readily hydrolysed by aqueous alcohol than 3-nitro-4-methoxybenzyl bromide. The order of reduction of the halogenated phenols with hydriodic acid in acetic acid solution: *p*-iodo > *o*-iodo > *p*-bromo > *o*-bromo > *p*-chloro, is also in accordance with the theory. The *m*-isomerides showed no tendency to be reduced, and of the chlorophenols only the *p*-compound showed any reduction. *ω-Bromo-*p*-toluoyl bromide*, b. p. 160—165°/14 mm., m. p. 39—40°, prepared by Davies and Perkin's method (T., 1922, **121**, 2202), yields ω-bromo-*p*-toluic acid, m. p. 223° (Zalkind, A., 1914, i, 957), on warming with formic acid. ω-Bromo-*m*-toluoyl bromide has b. p. 160—165°/14 mm., m. p. 23—25°. o-*Nitrobenzyl bromide*, light yellow plates, m. p. 45·5°, was obtained from *o*-nitrobenzyl chloride and phosphorus pentabromide. 3-*Nitro-4-hydroxybenzyl bromide*, yellow, prismatic needles, m. p. 82°, was obtained from dry hydrogen bromide and the alcohol in benzene solution. 3-*Nitro*-4-*methoxybenzyl bromide*, pale yellow needles, m. p. 108°, was similarly obtained from 3-nitro-4-methoxybenzyl alcohol. *m*-Bromophenol distils at 125—127°/12 mm. (cf. Diels and Bunzl, A., 1905, i, 431). R. B.

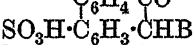
Solubility of 2 : 4 : 6-Trinitrotoluene, "Tetryl," and Tetranitroaniline in Organic Solvents. L. Desvergnes (*Mon. Sci.*, 1924, **14**, 121—130).—A detailed *résumé* of previous work by Taylor and Rinkenbach is given (A., 1923, i, 315, 320, 672). The solubility of 2 : 4 : 6-trinitrotoluene in 95% alcohol is 1·26 at 15°, 20·45 at 78·5°, and of trinitrophenylmethylnitroamine (tetryl) in water, 0·007 at 15°, 0·017 at 30°, 0·020 at 50°, 0·051 at 80°, 0·116 g. at 100°, per 100 g. of solvent in each case. A. C.

Specific Heats of Trinitrotoluene, "Tetryl," Picric Acid, and their Molecular Complexes. C. A. Taylor and W. H. Rinkenbach (*J. Amer. Chem. Soc.*, 1924, **46**, 1504—1510).—The following specific heats were determined by means of the Dewar liquid oxygen calorimeter, using lead as the standard of comparison. Tetryl, 0°, 0·213; 125°, 0·235; picric acid, 0°, 0·234; 120°, 0·337; trinitrotoluene, 0°, 0·309; 80°, 0·374; tetryl–picric acid compound, 0°, 0·254; 80°, 0·311; tetryl–trinitrotoluene compound, 0°, 0·287; 60°, 0·349. Intermediate specific heats are tabulated at 10° intervals, and equations deduced for the temperature–mean specific heat curves from $-182·8°$ to the highest temperature used for each substance. Kopp's law does not hold for trinitrotoluene, "tetryl," or picric acid. F. G. W.

Specific Heat and Thermal Diffusivity of certain Explosives. III. A. M. PRENTISS (*Army Ordnance*, 1924, 4, 242—246; cf. *ibid.*, 1923, 4, 184).—For trinitrotoluene, trinitroxylene, and trinitrophenylmethylnitroamine, respectively, the specific heats are: 0·3776 ($-200°$ to $+50°$), 0·3950 ($+20°$ to 50°), 0·4233 ($+20°$ to 50°); the coefficients of conductivity at 25° are: 0·00043, 0·00057, 0·00088, and the coefficients of diffusivity at 25°, 0·00197, 0·00225, and 0·00388, respectively. CHEMICAL ABSTRACTS.

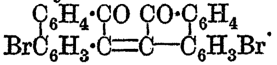
Derivatives of Tetrahydro- and Decahydro-naphthalenes. E. BŒDTKER and O. RAMBECH (*Bull. Soc. chim.*, 1924, [iv], **35**, 631—638).—The authors confirm the observation of Schroeter (D.R.-P. 333158) that aluminium chloride reacts with tetrahydronaphthalene at the ordinary temperature with formation of benzene and octahydro-anthracene and -phenanthrene, and demonstrate that the reaction is reversible. Methyltetrahydronaphthalene could not be obtained by the Friedel–Crafts reaction, but tetrahydro-2-ethylnaphthalene (b. p. 244°) was obtained in small yield. 2-iso*Propyltetrahydronaphthalene*, b. p. 255—256°, d_4^{16} 0·9518, n_D^{1} 1·5352, is obtained similarly from *n*-propyl chloride and tetrahydronaphthalene. The formation of 2-tert.-*butyltetrahydronaphthalene*, b. p. 265·5—266·5°, d_4^{15} 0·9463, n_D^{15} 1·5348, is accompanied by evolution of *iso*butane. 2-tert.-*Amyltetrahydronaphthalene* has b. p. 149·2—150°/12 mm., d_4^{17} 0·9478, n_D^{17} 1·5332, b. p. 280°/760 mm., with partial decomposition. When decahydronaphthalene is boiled with aluminium chloride, a mixture of saturated hydrocarbons, $C_{10}H_{18}$, b. p. 157—250°, is obtained.
F. G. W.

Bromine Compounds of Phenanthrene. III. H. HENSTOCK (*J. Chem. Soc.*, 1924, **125**, 1296—1299).—The bromination of potassium phenanthrene-2-sulphonate in aqueous solution yields a product giving a brilliant dark green *barium* salt, which in the absence of ammonium chloride changes almost instantaneously to a brown powder, normal *barium* 10-*bromo*-9-*hydroxyphenanthrene*-2-*sulphonate*. The green barium salt on acidifying with hydrochloric acid yields an *acid*, $C_{14}H_8OBr·SO_3H$, bright blue, amorphous powder, which is much more stable than the salt and probably possesses the constitution:



$$\begin{array}{l}\quad\;\; C_6H_4·CO \\ SO_3H·C_6H_3·CHBr\end{array}.$$

With dry bromine vapour, potassium phenanthrene-2-sulphonate is converted into an orange-yellow *dibromide*, $C_{14}H_9Br_2·SO_3K$, fuming in air through loss of hydrogen bromide, which on heating yields the yellow *potassium* 10-*bromo*-9-*hydroxyphenanthrene*-2-*sulphonate*. The free *acid*, granular, white powder, obtained from the *silver* salt, yields a colourless, doubly-refracting jelly with concentrated hydrochloric acid, and the bromine is therefore in position 10 (cf. Sandqvist, A., 1919, i, 120; 1920, i, 300). *Sodium, ferric, ammonium, basic* *barium*, $C_{14}H_7(OH)Br\cdot SO_3Ba(OH)$, *normal* and *basic lead* salts, $[C_{14}H_7(OH)BrSO_3]_8Pb_3$, are described. 9 : 10-*Dibromophenanthrene-2-sulphonyl bromide*, yellow, amorphous powder, has m. p. 204°. The scarlet substance previously obtained by treating 2 : 10-dibromophenanthrene with alcoholic potassium hydroxide (T., 1921, **119**, 59) has the composition $C_{28}H_{14}O_2Br_2$, yields *p*-bromodiphenic acid, m. p. 237—238° (cf. Schmidt and Junghans, A., 1904, i, 1033) on oxidation, and probably has the constitution



$$\begin{array}{l} \;\;C_6H_4\cdot CO\;\; CO\cdot C_6H_4 \\ \;\;\;|\qquad\;\;|\quad\;\;|\qquad\;| \\ BrC_6H_3\cdot C{=}C{-}C_6H_3Br \end{array}$$

R. B.

Space Lattice of Triphenylmethane. K. BECKER; H. MARK and K. WEISSENBERG.—(See ii, 449.)

Triphenylmethyl Fluoride. F. F. BLICKE (*J. Amer. Chem. Soc.*, 1924, **46**, 1515—1518).—*Triphenylmethyl fluoride*, m. p. 102—104°, was obtained by the action of acetyl fluoride on triphenylcarbinol suspended in benzene. It is much less reactive than the corresponding compounds of the other halogens, remaining unaffected after shaking for 24 hours in benzene solution, with 10 mols. of molecular silver, mercury, zinc, copper, bronze, or magnesium, and on boiling with excess of silver in benzene for 6 hours in an atmosphere of nitrogen. It is reduced by zinc chloride in ether, and oxidised by potassium permanganate in acetone, with quantitative formation of triphenylmethane and triphenylcarbinol, respectively. It condenses slowly with amines, and with magnesium phenyl bromide yields triphenylmethyl, triphenylcarbinol, and a red oil, but no tetraphenylmethane. F. G. W.

Action of Formaldehyde on Formylated Aromatic Amines and on Isatin. A. REISSERT and A. HÄNDELER (*Ber.*, 1924, **57**, [*B*], 989—996).—Formanilide is slowly converted by formaldehyde in aqueous alkaline solution into formic acid, and *formylmethylenedianiline*, $CHO\cdot NPh\cdot CH_2\cdot NHPh$, m. p. 93°, the constitution of which is established by its reduction with sodium amalgam to aniline, methylaniline, and formic acid; the *benzoyl* derivative has m. p. 119°. Boiling, aqueous potassium cyanide solution transforms formylmethylenedianiline into aniline, *anilinoacetamide*, m. p. 141°, anilinoacetic acid, and *anilinodiaceticmonoamide*, $CO_2H\cdot CH_2\cdot NPh\cdot CH_2\cdot CO\cdot NH_2$, m. p. 217°. *Formylmethylenedi-o-toluidine* has m. p. 108—109° (*benzoyl* derivative, m. p. 130°). *Formylmethylenedi-p-toluidine* has m. p. 92—93° (*benzoyl* derivative, m. p. 120—121°).

1-*Hydroxymethylisatin*, red crystals, m. p. 156—157°, is the main product of the interaction of equimolecular proportions of isatin and formaldehyde in boiling aqueous solution. The *oxime*, reddish-yellow needles, m. p. 138° (decomp.), *phenylhydrazone*, m. p. 180—181°, *acetate*, m. p. 112—113°, and *benzoate*, m. p. 124—125°, are described. *Methylenedi-isatin*, $\left[CO<\begin{smallmatrix}CO\\C_6H_4\end{smallmatrix}>N\right]_2CH_2$, a yellow, crystalline powder, decomp. 287° [*dioxime*, m. p. 230—231° (decomp.); *monophenylhydrazone*, decomp. 289—290°] is obtained as a by-product in the preparation of 1-hydroxymethylisatin. Isatic acid is converted by ice-cold formaldehyde solution into "*methylene-di-isatin hydrate*," $C_{17}H_{12}O_5N_2$, decomp. 262—264°, after darkening at 230°, the constitution of which has not been elucidated. It yields a *monoxime*, m. p. 208°, and is converted by boiling methyl alcohol into methylenedi-isatin. H. W.

Action of Potassium Cyanide on Aromatic Mustard Oils.

A. Reissert and K. Brüggemann (*Ber.*, 1924, **57**, [*B*], 981—989). —An extension of previous work (Reissert, A., 1904, i, 990).

Thio-oxanilonitrile is converted by benzoyl chloride and sodium carbonate into the corresponding N-*benzoyl* derivative,

NPhBz·CS·CN,

red needles, m. p. 103°, which is mixed with the *amide*, yellow needles, m. p. 218°, if sodium hydroxide is substituted for the carbonate. *Methylthio-oxanilonitrile* is a viscous, orange-coloured liquid, b. p. 160°/23 mm., from which methylaniline is obtained by the action of alkalis. Thio-oxanilothioamide, m. p. 98°, is readily prepared by the action of yellow ammonium sulphide on thio-oxanilonitrile. The latter substance is transformed by ethyl alcohol and hydrogen chloride in the presence of an inert solvent into *ethyl imidothio-oxanilate*, NHPh·CS·C:NH(OEt), yellow needles, m. p. 73°; the corresponding *hydrochloride*, m. p. 166°, is converted by alcohol into ethyl thio-oxanilate, m. p. 38—40°. Thio-oxanilonitrile is converted by aniline in boiling benzene into *phenylimido-oxanilonitrile*, NHPh·C(CN):NPh, m. p. 137°, the yield being poor. *Thio-oxalo*-o-*toluidinonitrile*, C_7H_7·NH·CS·CN, orange-coloured needles, m. p. 64°, is converted into the corresponding *benzoyl* derivative, m. p. 103°, the *amide*, yellow needles, m. p. 117°, and the *thioamide*, pale red needles, m. p. 90°. *Thio-oxalo*-p-*toluidinonitrile*, yellow needles, m. p. 127—128°, is converted by the methods used with the phenyl compound into the *benzoyl* derivative, m. p. 123°, *amide*, m. p. 169°, *thioamide*, m. p. 128°, *ethyl imidothio-oxalo*-p-*toluidinate*, C_7H_7·NH·CS·C:NH(OEt), m. p. 73° (*hydrochloride*, m. p. 166—167°), *ethyl thio-oxalo*-p-*toluidinate*, m. p. 82°, and *thio-oxalo*-p-*toluidinic acid*, m. p. 130°. *Thio-oxalo*-m-*xylidinonitrile*, yellow needles, m. p. 98°, yields the corresponding *amide*, m. p. 147°, *thioamide*, m. p. 136°, and *benzoyl* derivative, m. p. 104°. *Thio-oxalo-α-naphthylaminonitrile*, pale red needles, m. p. 136°, gives rise to the corresponding *amide*, m. p. 199°, and *thioamide*, m. p. 147°; the *benzoyl* derivative, red needles, m. p. 135°, is converted by exposure to sunlight into the colourless *dimeride*, m. p. 165—166°. *Thio-oxalo-β-naphthylaminonitrile* crystallises in yellow needles, m. p. 157°.

The action of hydrogen peroxide on the thionitriles leads mainly to the production of derivatives of oxamide. The thioamides are converted by potassium ferricyanide into thiazole derivatives, of which the following are described: 3-*methylbenzthiazole*-1-*carboxylamide*, m. p. 163°, and the corresponding *acid*, m. p. 110—111°; 5-*methylbenzthiazole*-1-*carboxylamide*, m. p. 243°, the corresponding *acid*, m. p. 110—111° (decomp.), and its *silver* salt and *methyl* ester, m. p. 96°; 3:5-*dimethylbenzthiazole*-1-*carboxylamide*, m. p. 192°, and the corresponding *acid*, m. p. 114°; *α-naphththiazole*-1-*carboxylamide*, m. p. 210°, and *α-naphththiazole*-1-*carboxylic acid*, m. p. 129—130°.

H. W.

Salts of Phenyldiguanidine. E. ROMANI (*Caoutchouc et Gutta-Percha*, 1923, **20**, 12005—12008).—An investigation of the utility of derivatives of guanidine as accelerators for the vulcanisation of caoutchouc. *α-Phenyldiguanidine carbonate*, R_2,H_2CO_3 [where $R{=}NH{:}C(NHPh){\cdot}NH{\cdot}C(NH_2){:}NH$], has m. p. 128—130°; *carbamide*, m. p. 216—218°; *hydrosulphide*, R,H_2S, m. p. 155°; *polysulphide*, R_2,H_2S_2, m. p. 209—210°; *thiocyanate*, $R,HSCN$, nacreous, m. p. 232°; *thiocarbamide*, m. p. 142—143°. *Phenyldiguanidinoethylthiocarbamide* has m. p. 246°; *phenyldiguanidinophenylthiocarbamide* was prepared. *Phenyldiguanidine dithiocarbamate* has m. p. 106°; *dithiophenylcarbazinate*, m. p. 142°; *piperidyldithiocarbamate*, m. p. 94—95°; *phenyldithiocarbamate*, m. p. 140°; *ethylxanthate*, pale yellow, m. p. 128°; *dithiopyromucate*, garnet red, m. p. 158°; *mercaptobenzthiazole* compound, yellow, m. p. 160; *zincate* (cf. Cohn, A., 1911, i, 928).

CHEMICAL ABSTRACTS.

Action of Carbon Dioxide on Phenoxides. H. MEYER (*Z. anal. Chem.*, 1924, **64**, 72—81).—The passage of carbon dioxide through solutions of alkali phenoxides at 0° produces crystalline precipitates consisting of definite compounds of the free phenol with the alkali phenoxide. Some of these substances may be purified by recrystallisation from organic solvents whilst others are decomposed in these media into the phenol which dissolves and the alkali phenoxide which remains insoluble. The following compounds have been prepared: $PhOK,3PhOH$, long, thin, colourless needles, m. p. 114°; $p\text{-}C_6H_4Me{\cdot}OK,3p\text{-}Me{\cdot}C_6H_4{\cdot}OH$, m. p. 148°; $o\text{-}NO_2{\cdot}C_6H_4{\cdot}OK,o\text{-}NO_2{\cdot}C_6H_4{\cdot}OH,3H_2O$, golden-yellow leaflets, $o\text{-}NO_2{\cdot}C_6H_4{\cdot}ONa,o\text{-}NO_2{\cdot}C_6H_4{\cdot}OH,6H_2O$, red crystals, and

$$o\text{-}NO_2{\cdot}C_6H_4{\cdot}ONH_4,o\text{-}NO_2{\cdot}C_6H_4{\cdot}OH,H_2O,$$

yellowish-brown leaflets; $m\text{-}NO_2{\cdot}C_6H_4{\cdot}OK,2m\text{-}NO_2{\cdot}C_6H_4{\cdot}OH,5H_2O$, brown crystals decomposed on warming;

$$p\text{-}NO_2{\cdot}C_6H_4{\cdot}OK,p\text{-}NO_2{\cdot}C_6H_4{\cdot}OH,3H_2O,$$

short, thick, ochre-yellow needles, m. p. 170° (decomp.),

$$2p\text{-}NO_2{\cdot}C_6H_4{\cdot}ONa,3p\text{-}NO_2{\cdot}C_6H_4{\cdot}OH,3H_2O,$$

thick, brownish-yellow needles, m. p. 156° (decomp.),

$$p\text{-}NO_2{\cdot}C_6H_4{\cdot}ONH_4,p\text{-}NO_2{\cdot}C_6H_4{\cdot}OH,H_2O,$$

small yellow leaflets, m. p. 126—130° (decomp.); from 3-nitro-*p*-cresol, $NO_2{\cdot}C_7H_6{\cdot}OK,5NO_2{\cdot}C_7H_6{\cdot}OH,8H_2O$, reddish-brown crystals, m. p. 53°, $NO_2{\cdot}C_7H_6{\cdot}ONa,7NO_2{\cdot}C_7H_6{\cdot}OH,8H_2O$,

$$NO_2{\cdot}C_7H_6{\cdot}ONH_4,2NO_2{\cdot}C_7H_6{\cdot}OH,4H_2O,$$

yellow powder, m. p. 140° (decomp.);

$$\alpha\text{-}C_{10}H_7{\cdot}OK,4\alpha\text{-}C_{10}H_7{\cdot}OH,5H_2O,$$

green, amorphous powder; $\beta\text{-}C_{10}H_7{\cdot}OK,2\beta\text{-}C_{10}H_7{\cdot}OH,5H_2O$, colourless crystals; from pyrocatechol, $OH{\cdot}C_6H_4{\cdot}OK,C_6H_4(OH)_2,2H_2O$, colourless crystals, $2OH{\cdot}C_6H_4{\cdot}ONa,C_6H_4(OH)_2,6H_2O$, colourless, glistening crystals; from quinol, colourless crystals,

$$OH{\cdot}C_6H_4{\cdot}OK,7C_6H_4(OH)_2$$

and $OH\cdot C_6H_4\cdot ONa,4C_6H_4(OH)_2$; from guaiacol,

$OMe\cdot C_6H_4\cdot OK,OMe\cdot C_6H_4\cdot OH,1\cdot 5H_2O$,

large colourless needles, m. p. 186° (decomp.),

$2OMe\cdot C_6H_4\cdot ONa,5OMe\cdot C_6H_4\cdot OH,2H_2O$,

colourless crystals, m. p. 139°; from 4-nitroguaiacol,

$OMe\cdot C_6H_3(NO_2)OK,OMe\cdot C_6H_3(NO_2)\cdot OH,3H_2O$,

yellow crystals, m. p. 169—171°; from 5-chloroguaiacol,

$OMe\cdot C_6H_3Cl\cdot OK,OMe\cdot C_6H_3Cl\cdot OH,2H_2O$,

yellowish-white, very stable needles, m. p. 146°. In purifying phenols by the carbon dioxide method, the substance should be dissolved in sodium hydroxide and the gas passed through the warm solution for a prolonged period to avoid contamination of the precipitate by complex compounds. A. R. P.

Sulphonation of *m*-Cresol and its Methyl Ether. R. D. HAWORTH and A. LAPWORTH (*J. Chem. Soc.*, 1924, **125**, 1299—1307; cf. T., 1923, **123**, 2982).—The sulphonation of *m*-cresol with concentrated sulphuric acid at 30—35° yields *m*-cresol-4- and -6-sulphonic acids in the ratio 1 : 2·7; the 6-sulphonic acid is also the main product at 120° (cf. Claus and Krauss, A., 1888, 280). The acids were separated by means of their barium salts and identified by methylation of the potassium salts to the corresponding 3-methoxytoluenesulphonates.

[With M. L. WILSON.]—Sulphonation with chlorosulphonic acid (1 mol.) in carbon disulphide at −15° yields potassium *m*-tolyl sulphate (Verley, A., 1901, i, 143) and potassium *m*-cresol-6-sulphonate. In the presence of pyridine, 70% of the theoretical yield of potassium *m*-tolyl sulphate was obtained. On heating the mixture at 100°, after distilling off the carbon disulphide, *m*-cresol-6-sulphonic acid alone was obtained. The *barium* (decomp. 180°), *ammonium*, *ferrous*, *zinc*, and *potassium* salts of *m*-cresol-6-sulphonic acid are described, and the *barium* (decomp. 150°), *copper*, and *potassium* salts of *m*-cresol-4-sulphonic acid. With 2 or 3 mols. of chlorosulphonic acid below 35° *m*-cresol yields *m*-cresol-4 : 6-disulphonic acid (*barium* salt), the product, after distilling off the carbon disulphide, being heated at 100° to ensure migration of the sulphonic group to the nucleus. No *m*-cresolsulphonyl chloride was produced. Sulphonation of *m*-tolyl methyl ether with chlorosulphonic acid at −15° gave only 3-methoxytoluene-6-sulphonic acid in good yield. Nitration of potassium *m*-cresol-6-sulphonate in acetic acid gives *potassium 4-nitro-*m*-cresol-6-sulphonate*, pale yellow prisms, potassium 6-nitro-*m*-cresol-4-sulphonate being similarly obtained from the 4-sulphonate. Both nitro compounds on heating with hydrochloric acid in a sealed tube yield the corresponding nitrocresol. Oxidation of potassium 3-methoxytoluene-6-sulphonate with potassium permanganate yields the *potassium hydrogen 3-methoxy-6-sulphobenzoate*, whereas oxidation of the corresponding sulphonamide yields *5-methoxy-*o*-benzoicsulphinide*, m. p. 242°, also prepared from the potassium hydrogen salt. Potassium 3-methoxytoluene-4-sulphonate similarly yields the *potassium hydrogen 3-methoxy-4-sulphobenzoate* and *3-methoxy-4-sulphamido-*

benzoic acid, m. p. 254—255°, which is also obtained by the oxidation of 3-methoxytoluene-4-sulphonamide with alkaline permanganate. 3-Methoxytoluene-2-sulphonamide similarly yields 3-*methoxy*-o-*benzoicsulphinide*, m. p. 227—228° (decomp.).

R. B.

o-Hordenine [o-β-Dimethylaminoethylphenol]. J. VON BRAUN and O. BAYER (*Ber.*, 1924, **57**, [*B*], 913—914).—Benz-*o*-β-chloroethylanilide is converted by dimethylamine in benzene solution at 100° into *benz*-o-β-*dimethylaminoethylanilide*,

$NMe_2\cdot[CH_2]_2\cdot C_6H_4\cdot NHBz$,

m. p. 95°; the hygroscopic *hydrochloride* and the *picrate*, m. p. 160°, are described. It is hydrolysed by hydrochloric acid at 150° to o-β-*dimethylaminoethylaniline*, b. p. 129°/12 mm., m. p. 45°, which yields a very hygroscopic *hydrochloride* and a *chloroplatinate*, decomp. 209°. The base is converted through the diazonium compound into o-β-*dimethylaminoethylphenol*, a pale yellow liquid, b. p. 136—137°/13 mm., which could not be caused to crystallise; the hygroscopic *hydrochloride*, *chloroplatinate*, m. p. 144°, *sulphate*, *picrate*, m. p. 142°, and quaternary methiodide, m. p. 218°, are described. The physiological action of *o*-β-dimethylaminoethylphenol is much weaker than that of hordenine. H. W.

Catalytic Hydrogenation of p- and o-Hydroxydiphenyl. J. RANEDO and A. LEÓN (*Anal. Fís. Quím.*, 1924, **22**, 222—232; cf. A., 1923, i, 909).—Catalytic perhydrogenation of *p*-hydroxydiphenyl in presence of platinum black yields two isomerides identical with those obtained from *o*-*cyclo*hexylphenol by Schrauth and Görig (A., 1923, i, 1084). Perhydrogenation of *o*-hydroxydiphenyl yields a cyclo*hexyl*cyclo*hexanol* having b. p. 172—177°/75 mm., m. p. 63°. By oxidation a ketone is obtained identical with that obtained by Schrauth and Görig from the oxidation of the above isomerides. G. W. R.

Lichen Products. IV. Synthesis of Divarinol. A. SONN and B. SCHEFFLER (*Ber.*, 1924, **57**, [*B*], 959—961).—Methyl 3 : 5-dimethoxybenzoate is condensed with ethyl acetate and sodium to ethyl 3 : 5-dimethoxybenzoylacetate, b. p. 189—191°/28 mm., which is methylated with sodium ethoxide and methyl sulphate and then submitted to simultaneous ketonic fission and reduction by Clemmensen's method, thus yielding 3 : 5-dimethoxypropylbenzene, b. p. 147—148°/29 mm. (cf. Mauthner, this vol., i, 524). The latter substance is more readily obtained by treating the fraction of beechwood tar, b. p. 265—295°, with hot potassium hydroxide solution, whereby a mixture of the potassium salts of 5-*n*-propylpyrogallol mono- and di-methyl ethers separates. This, on methylation, gives 5-*n*-propylpyrogallol trimethyl ether, b. p. 263—265°, which is reduced by sodium and alcohol to 3 : 5-dimethoxypropylbenzene, b. p. 145—147°/27 mm. The latter substance is converted by hydriodic acid (*d* 1·7) into divarinol. Myristicin is also converted by sodium and alcohol into divarinol. The introduction of the aldehydic group into divarinol by Gattermann's method gives a *substance*, b. p. 184—185°. H. W.

Effect of Temperature and of Medium in the Dehydration of α-Phenylethyl Alcohol. R. DESCAMPS (*Bull. Soc. chim. Belg.*, 1924, **33**, 139—145; cf. Wuyts, A., 1921, i, 506).—In the dehydration of α-phenylethyl alcohol by means of *p*-toluenesulphonic acid in the absence of a solvent, the proportion of styrene obtained decreases with temperature, *e.g.*, 7·31% at 82·6°, 0·8% at 48·4°. Camphorsulphonic acid under similar conditions produces a smaller proportion of the hydrocarbon, whilst in presence of benzene as solvent the proportion is increased. In presence of carbon disulphide at 48·4°, the proportion of alcohol converted into styrene is 0·58%. The yield of ether in all the cases studied was good.

H. J. E.

Tervalent Carbon. II. Conversion of the Ethers of Tertiary Alcohols into Organic Potassium Compounds and Hexa-substituted Ethane Derivatives. K. ZIEGLER and B. SCHNELL (*Annalen*, 1924, **437**, 227—255; cf. this vol., i, 308).—The reaction of triphenylmethyl alkyl ethers with potassium (A., 1923, i, 921) has now been utilised in the conversion of tertiary ethers into hexa-substituted ethanes. Diphenylalkylcarbinols, $OH{\cdot}CPh_2R$, in cold methyl-alcoholic solution in the presence of 2% of sulphuric acid (cf. this vol., i, 509) are converted into the corresponding methyl ethers. At higher temperatures the ethers are converted into ethylene derivatives, showing that this is the final stage of the reaction. Confirmation of this conclusion is found in the fact that αα-diphenylpropylene is unchanged by methyl alcohol. With phenyldialkylcarbinols the reaction is slower and the ethers must be prepared at higher temperatures with consequent loss of yield. When the corresponding chloride is available, *e.g.*, β-phenyl*iso*propyl chloride, the ether can be obtained in good yield by the action of methyl alcohol. On shaking with potassium in cold ethereal solution, the diphenyl tertiary ethers are converted into potassium compounds: $CPh_2R{\cdot}OMe \longrightarrow CPh_2R{\cdot}K$. Phenyl tertiary ethers, *e.g.*, phenyldibenzylmethyl methyl ether,

$$CPh(CH_2Ph)_2{\cdot}OMe,$$

and β-phenyl*iso*propyl methyl ether, $CPhMe_2{\cdot}OMe$, react less readily and ethers such as *tert.*-butyl methyl ether, terpineol methyl ether, and camphene hydrate methyl ether, in which no phenyl group is attached to the tertiary carbon atom, are not attacked by potassium. On treatment with tetramethylene dibromide, these potassium compounds are decomposed, yielding hexa-substituted ethanes: $CPh_2R \ldots K \longrightarrow ({\cdot}CPh_2R)_2$, and in some cases the reverse reaction takes place on treating the substituted ethane with potassium. The dissociation capacity of the substituted ethanes is discussed in relation to the valency considerations advanced by Wieland, Meerwein, and Skraup.

αα-Diphenylethyl methyl ether, $CPh_2Me{\cdot}OMe$, white needles, m. p. 35—36°, yields *potassium αα-diphenylethyl*, brick-red powder, which with carbon dioxide gives 80—90% of the theoretical yield of αα-diphenylpropionic acid, and with benzyl chloride yields *αββ-triphenylpropane*, $CPh_2Me{\cdot}CH_2Ph$, dense prisms, m. p. 116—117°.

With tetramethylene dibromide in the cold, the potassium compound yields ββγγ-*tetraphenylbutane*, m. p. 126—127°. On heating, its carbon tetrachloride solution becomes unsaturated and takes up bromine, yielding ββ-diphenylvinyl bromide, in consequence of decomposition into αα-diphenylethane and αα-diphenylethylene. αα-*Diphenylpropyl methyl ether*, $CPh_2Et\cdot OMe$, dense, triangular plates, m. p. 68—69°, yields *potassium* αα-*diphenylpropyl*, red oil, converted into αα-diphenylbutyric acid by carbon dioxide. γγδδ-*Tetraphenylhexane*, m. p. 85—86°, obtained from this potassium compound, gradually dissociates in solution but no satisfactory reaction constant was obtained. The cold, freshly-prepared solution in carbon disulphide is saturated, but gradually becomes unsaturated and 1 mol. of bromine is taken up. ααβ-*Triphenylethyl methyl ether*, $CH_2Ph\cdot CPh_2\cdot OMe$, flat, sword-like cusps or radial prisms, m. p. 93—94°, gives *potassium* ααβ-*triphenylethyl*, small, brown crystals with blue lustre, yielding ααβ-triphenylpropionic acid (this vol., i, 171) with carbon dioxide and αββ-triphenylpropane on treatment with methyl iodide. Attempts to obtain αββγγδ-hexaphenylbutane were unsuccessful, and only resinous substances were formed, evidently mixtures of the two decomposition products ααβ-triphenylethane and ααβ-triphenylethylene. *Diphenyl*cyclo*hexylmethyl methyl ether*, $C_6H_{11}\cdot CPh_2\cdot OMe$, laminated prisms, m. p. 69—70°, yields *potassium diphenyl*cyclo*hexylmethyl*, bright red, which with alcohol is converted into diphenyl*cyclo*hexylmethane and with carbon dioxide gives *diphenyl*cyclo*hexylacetic acid*, microcrystalline powder, m. p. 202—203°. Tetramethylene dibromide converts the potassium compound into a sparingly soluble colourless *substance* which is probably ααββ-tetraphenyl-αβ-di*cyclo*hexylethane. This substance in chloroform solution readily absorbs bromine, iodine, and oxygen, yielding in the latter case a thick oil, probably a peroxide. Treatment with potassium–sodium alloy yields the original potassium diphenyl*cyclo*hexylmethyl. αββ′-*Triphenyl*iso*propyl methyl ether*, lustrous needles, m. p. 105—106°, gives a brownish-violet *potassium* αββ′-*triphenyl*iso*propyl*, which with carbon dioxide yields αββ′-*triphenyl*iso*butyric acid*,

$$(PhCH_2)_2CPh\cdot CO_2H,$$

m. p. 125—126°, and with tetramethylene dibromide, αβγδ-tetraphenyl-βγ-dibenzylbutane, m. p. 126—127°, which shows no tendency to dissociate in solution. β-*Phenyl*iso*propyl methyl ether*, from β-phenyl*iso*propyl chloride, colourless oil, b. p. 78°/13 mm., with an odour resembling camphor and peppermint, gives the deep red *potassium* β-*phenyl*iso*propyl*, which with carbon dioxide yields α-phenyl*iso*butyric acid. R. B.

Thiophenols. VI. Thiophenol Ethers of Triphenylmethane and the Bathochromic Action of Alkylthiol Groups. K. Brand and O. Stallmann (*J. pr. Chem.*, 1924, [ii], **107**, 358—382).—The corresponding carbinol (A., 1921, i, 664) is reduced by zinc and acetic acid to *o-methylthioltriphenylmethane*, colourless tablets, m. p. 111°. This combines with methyl sulphate to form a *sulphonium methyl sulphate*, $CHPh_2\cdot C_6H_4\cdot SMe_2\cdot SO_4Me$, colourless scales,

m. p. 163°; the corresponding *iodide* is very unstable. o-*Methylthioltriphenylmethyl chloride,* formed when the carbinol is treated with ethereal hydrogen chloride, crystallises in needles, m. p. 126°, and yields unstable coloured compounds with ferric and stannic chlorides. oo′-*Dimethylthioltriphenylmethane,* m. p. 100·5°, was obtained satisfactorily by reducing the corresponding carbinol, not with zinc and acetic acid, but with alcoholic hydrogen chloride (Kaufmann, A., 1912, i, 351). The corresponding *chloride* forms fine needles, m. p. 164° (decomp.), and also yields unstable compounds with ferric and stannic chlorides. oo′o″-*Trimethylthioltriphenylcarbinol* is formed by interaction of magnesium *o*-methylthiolphenyl bromide and methyl *o*-methylthiolbenzoate; it crystallises from alcohol in prisms, m. p. 180°, but from chloroform or benzene in octahedra, m. p. 190°. It yields the corresponding *methane* derivative, m. p. about 176°, and *chloride,* colourless rods, m. p. 140° (decomp.).

p-Methylthioltriphenylcarbinol is formed together with much *pp*′-dimethylthioldiphenyl, by interaction of magnesium *p*-methylthiolphenyl bromide and benzophenone (cf. Bistrzycki and Kuba, A., 1922, i, 33). By methods analogous to those described above, the following *p*-substituted derivatives were prepared: pp′-*dimethylthioltriphenylcarbinol,* forming needles, m. p. 110—111°, and yielding a *perchlorate,* bronzy needles, m. p. 195° (decomp.), and *double chlorides* with mercuric chloride (green needles, m. p. 122°, decomposed by water) and stannic chloride (green needles, m. p. 205—207°, unstable); pp′-*dimethylthioltriphenylmethane,* needles, m. p. 63°; pp′-*dimethylthioltriphenylmethyl chloride,* m. p. 122°; pp′p″-*trimethylthioltriphenylcarbinol* (the requisite methyl *p*-methylthiolbenzoate was obtained from *p*-cyanophenyl methyl sulphide), colourless needles, m. p. 128°, yielding a *perchlorate,* bright bronze rods, m. p. 220° (decomp.), and *double* salts with mercuric chloride (bronzy-green needles, m. p. 163—165°) and stannic chloride (prisms, m. p. about 210°). The corresponding *methane* forms colourless needles, m. p. 95·5°; *chloride,* m. p. 152°. Various colour reactions of all these substances are described.

oo′-*Dimethylthioldiphenyl* was prepared by treating *o*-iodophenyl methyl sulphide with copper bronze at 200—250°; it forms feathery crystals, m. p. 158·5°. W. A. S.

Thiophenols. VII. Simple Method of preparing *p*-Methylthiol- and *pp*′-Dimethylthiol-triphenylcarbinols. K. Brand and W. Vogt (*J. pr. Chem.*, 1924, [ii], **107**, 383—390).—By reactions resembling those of Döbner's malachite-green synthesis, phenyl methyl sulphide heated with benzophenone chloride and aluminium chloride in carbon disulphide solution yields *p*-methylthioltriphenylcarbinol, and with benzotrichloride and zinc chloride, *pp*′-dimethylthioltriphenylcarbinol (cf. preceding abstract). When equimolecular proportions of phenyl methyl sulphide and benzotrichloride are used, the product is p-*methylthiolbenzophenone,* m. p. 72—73°, which yields two *oximes,* m. p. 138° and 105°, respectively.

p-Methylthioltriphenylcarbinol gives violet-red, and *pp'*-dimethylthioltriphenylcarbinol bluish-green salts with mineral acids.

W. A. S.

Action of Organo-magnesium Compounds on Nitriles. E. ECTORS (*Bull. Soc. chim. Belg.*, 1924, **33**, 146—159).—Benzonitrile acts on magnesium methyl bromide with formation of acetophenone (80% yield) together with *s*-triphenylpyridine; with magnesium ethyl bromide it yields phenyl ethyl ketone, no other product being isolated. With magnesium benzyl chloride, it forms phenyl benzyl ketone, the dimeride of phenyl benzyl ketimine, and a third substance, $C_{21}H_{18}N_2$. The dimeride is shown to be 3 : 4 : 5 : 6-*tetraphenylhexahydro*-1 : 2-*diazine*, fine needles, m. p. 192°, whilst the third product proved to be 3 : 4 : 5-*triphenylpyrazoline*, m. p. 152°, *hydrochloride*, m. p. 221° (decomp.). Benzonitrile is differentiated from aliphatic compounds such as phenylacetonitrile in its action on organo-magnesium compounds by the formation of such condensation products in addition to the high yield of ketone obtained (cf. Blaise, A., 1912, i, 164). H. J. E.

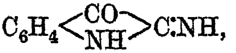
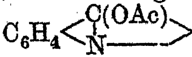
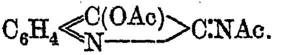
Reaction Velocity of Rearrangement of Potassium Dibenzhydroxamate. G. DOUGHERTY and L. W. JONES (*J. Amer. Chem. Soc.*, 1924, **46**, 1535—1539).—The rearrangement of potassium dibenzhydroxamate (5·5 g. per litre) under the influence of an equivalent of potassium hydroxide, at 25°, is unimolecular for the last 75% of the reaction period, and is represented by the scheme $COPh\cdot NK\cdot O\cdot COPh \longrightarrow COPh\cdot OK + COPh\cdot N\colon$; $COPh\cdot N\colon \longrightarrow NPh\colon C\colon O$. The apparent deviation during the first 25% of the reaction time is due to the hydrolysis of the dibenzhydroxamic acid to monobenzhydroxamic and benzoic acids, the consequent increase in acidity of the reaction mixture, above that required by the actual rearrangement, ceasing as the unimolecular reaction constant assumes a steady value. F. G. W.

Correlation of Additive Reactions with Tautomeric Change. III. The Cyano-imino Additive Process. E. H. INGOLD (*J. Chem. Soc.*, 1924, **125**, 1319—1322).—α-Cyano-β-imino-α-phenyl-β-*o*-tolylethane on treatment with alcoholic sodium ethoxide readily undergoes degradation to phenylacetonitrile and *o*-toluonitrile: $C_7H_7\cdot C(\colon NH)\cdot CHPh\cdot CN \longrightarrow CH(H)Ph\cdot CN + C_7H_7\cdot CN$, a balanced reaction resulting. Some cyanobenzyline was also obtained from the hydrochloric acid extract. Ethyl α-cyano-β-imino-β-phenylpropionate similarly yields ethyl cyanoacetate and benzonitrile, but the equilibrium between ethyl cyanoacetate and ethyl cyanoiminoglutarate is disturbed by reactions leading to ethyl α-cyano-β-iminobutyrate: $2CH_2(CN)\cdot CO_2Et \rightleftharpoons CO_2Et\cdot CH_2C(\colon NH)\cdot CH(CN)\cdot CO_2Et \longrightarrow Me\cdot C(\colon NH)\cdot CH(CN)\cdot CO_2Et$. This reversibility of the cyano-imino additive process is in accordance with Usherwood's views of tautomeric change (T., 1923, **123**, 1717).

R. B.

Reduction Products of *o*-Nitromandelonitrile. A. REISSERT and K. HESSERT (*Ber.*, 1924, **57**, [*B*], 964—972).—Reinvestigation of the substance obtained by Heller (A., 1906, i, 585) by the reduction of *o*-nitromandelonitrile and regarded by him as a compound of the quinhydrone type composed of $N(OH)_2 \cdot C_6H_4 \cdot CH(OH) \cdot CN,HCl$ and $OH \cdot NH \cdot C_6H_4 \cdot CH(OH) \cdot CN,HCl$, leads the authors to the conclusion that it is *o*-hydroxylaminomandelamide hydrochloride.

The mode of preparation and the properties of the compound are in complete harmony with Heller's description. The substance is decomposed by warm water into isatin and *anthroxanamide*, m. p. 211—212° (considered erroneously by Heller as nitrosomandelonitrile); with acetylating agents, it yields isatin and 1-acetoxyisatin in varying amount, whilst with phenylhydrazine it gives isatin-1- and -2-phenylhydrazones and 1-hydroxyisatin-3-phenylhydrazone. The formation of derivatives of 1-hydroxyisatin is completely in accord with Heller's conception of the partial reduction of the nitro group; since, however, exactly two atomic proportions of hydrogen are used, it appears reasonable to attribute their production to intermolecular oxidation, which should therefore be accompanied by the formation of dihydroxyindole as observed by Heller and Sourlis (A., 1908, i, 208), but not by the authors.

o-Hydroxylaminomandelamide hydrochloride is converted by sodium carbonate and sodium hydroxide into *isatin-2-imide*,  $C_6H_4<\begin{smallmatrix}CO\\NH\end{smallmatrix}>C{:}NH$, golden-yellow needles, m. p. 147—148° (decomp.). It is readily hydrolysed by dilute acids into isatin and ammonia, and by alkali hydroxide to isatic acid and by aniline into isatin-2-anilide. It is easily converted into *isatin-2-phenylhydrazone*, m. p. 222°, *isatin-2-semicarbazone*, m. p. 235—236°, and *isatindioxime*, m. p. 182—183° (decomp.). Treatment of *o*-hydroxylaminomandelamide or isatin-2-imide with sodium acetate and acetic anhydride gives a *diacetyl* compound, m. p. 224—225° (decomp.) after darkening at 200°, which is regarded as an isatol derivative,  $C_6H_4<\begin{smallmatrix}C(OAc)\\N\end{smallmatrix}>C{:}NAc$ or  $C_6H_4\ll\begin{smallmatrix}C(OAc)\\N\end{smallmatrix}>C{:}NAc$. It is hydrolysed in well-marked stages to a *monoacetyl* compound, m. p. 281—282° (decomp.) after darkening at 240°, which does not exhibit ketonic properties, and ultimately to isatin.

o-Hydroxylaminobenzoic acid (cf. Bamberger and Pyman, A., 1909, i, 573) is conveniently prepared by treating *o*-nitrobenzaldehyde with sodium hydrogen sulphite and potassium cyanide and subsequently warming the solution at 60°.

Cautious oxidation of Kalle's "anhydrohydroxylaminomandelic acid" (cf. Heller, *loc. cit.*) appears to lead to the formation of 1-hydroxyisatin, which, however, could be isolated only as the phenylhydrazone. H. W.

Constitution of and Method of preparing Hydroxyphenylhomocampholic Acid. A. HALLER and L. PALFRAY (*Compt. rend.*, 1924, **178**, 1647—1652).—From dibenzoylcamphor, 1-hydroxy-2-benzoylcamphene (Forster, T., 1901, **79**, 987) was prepared and either fused with potassium hydroxide at 195—200° (yield about

30% of theory) or heated at 200—220° with alcoholic sodium hydroxide (yield about 60%) or with a mixture of acetic and hydrochloric acids (yield about 50%) or with 50% sulphuric acid; it was thus converted (cf. cyanocamphor, Haller and Weimann, A., 1907, i, 278) into benzoylcampholic acid. This also is obtained directly, together with hydroxybenzoylcamphene, by treating dibenzoylcamphor with alcoholic sodium hydroxide (2 mols.) at 200—210°. The product is identical in all respects with that obtained from methyl cyanocampholate (*loc. cit.*). When reduced with sodium amalgam, it gives phenylhydroxyhomocampholic acid, identical with Haller and Minguin's product (A., 1900, i, 452). The hydroxy group is thus again proved to be attached to the same carbon atom as the phenyl radical, not to the adjacent one, as stated by Rupe and Blechschmidt (A., 1918, i, 222).

W. A. S.

δ-Ketonic Nitriles and their Relation to Cyclic Compounds. III. E. P. KOHLER and C. F. H. ALLEN (*J. Amer. Chem. Soc.*, 1924, **46**, 1522—1534).—Phenylacetonitrile condenses with phenyl styryl ketone in presence of sodium methoxide with formation of two stereoisomeric γ-*cyano*-βγ-*diphenylbutyrophenones*,

$$CN{\cdot}CHPh{\cdot}CHPh{\cdot}CH_2{\cdot}COPh \text{ (I)},$$

prisms, m. p. 118° (*a*), and 109° (*b*), respectively, (*b*) being converted into (*a*) on saturating a solution of the former in chloroform or carbon tetrachloride with hydrogen bromide. The *methyl* esters of the corresponding stereoisomeric *acids* form needles, m. p. 150° and 139° respectively, and are both hydrolysed to the same γ-*benzoyl*-αβ-*diphenylbutyric acid*, needles, m. p. 239°, which on re-esterification gives only the ester of m. p. 150°. The action of alcoholic potassium hydroxide on the nitriles (I) affords a *substance*, $C_{38}H_{31}O_2N$, microscopic needles, m. p. 257°, which is also formed together with (I) in the above condensation. On saturating a solution of either of the isomerides (I) in glacial acetic acid with hydrogen bromide, 2-*keto*-3 : 4 : 6-*triphenyltetrahydropyridine*, needles, m. p. 173°, was obtained, and this yielded 2-*hydroxy*-3 : 4 : 6-*triphenylpyridine*, fluorescent prisms, m. p. 263°, on treatment with sodium nitrite in glacial acetic acid. Bromination of the isomeride (*b*) in glacial acetic acid afforded 2-*bromo*-3 : 4 : 6-*triphenylpyridine*, fluorescent needles, m. p. 110°, from which, by the action of sodium butoxide, 2-*butoxy*-3 : 4 : 6-*triphenylpyridine*, small needles, m. p. 94°, was obtained. In chloroform, bromination yielded, together with the above product, 2-*bromo*-6-*hydroxy*-3 : 4 : 6-*triphenyl*-5 : 6-*dihydropyridine*, colourless needles, m. p. 100° (*benzoyl* derivative, pointed rods, m. p. 137°), together with 2-bromo-3 : 4 : 6-triphenylpyridine, the latter being also formed by the action of methyl-alcoholic potassium acetate solution or hydrogen bromide in glacial acetic acid. The nitrile (*b*) when brominated in chloroform gave γ-*bromo*-γ-*cyano*-βγ-*diphenylbutyrophenone*, $CN{\cdot}CBrPh{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$ (IV), in two stereoisomeric forms, plates, m. p. 172° and 131°, respectively. The latter was slowly converted into the former by the action of hydrogen bromide in glacial acetic acid, further action yielding 2-bromo-3 : 4 : 6-triphenylpyridine. On boiling (IV) with methyl-alcoholic potassium acetate solution, two stereoisomeric 2-*cyano*-1-*benzoyl*-2 : 3-*diphenyl* cyclo*propanes*, prisms, m. p. 172° and 143°, respectively, were produced, a third isomeride, fine needles, m. p. 178°, b. p. 275°/29 mm., being obtained by prolonged action. The cyano group is completely inactive in all three isomerides. The isomeride of m. p. 172° was reduced to the nitrile (*b*) by the action of zinc dust in glacial acetic acid, the other isomerides yielding the nitrile (*a*). The action of methyl-alcoholic potassium hydroxide produced two stereoisomeric β-*cyano*-γ-*hydroxy*-βγ-*diphenylbutyrophenones*, stout needles, m. p. 156° (*c*) and 218° (*d*), respectively, the former being obtained from the isomeride of m. p. 172°, the latter from the others. The compound (*c*) was converted into (*d*) by solution in glacial acetic acid, the reverse change being effected by the action of methyl-alcoholic hydrogen chloride. Both isomerides yielded the hydrated *acetate*, $C_{25}H_{21}O_3N,H_2O$, stout needles, m. p. 121°, which yielded the anhydrous *acetate*, $C_{25}H_{21}O_3N$, microcrystalline plates, m. p. 142°, on boiling with acetyl chloride. On oxidation, α-*cyano*-αβ-*dibenzoyl*-α-*phenylethane*, prisms, m. p. 206°, was produced. β-Cyano-γ-hydroxy-βγ-diphenylbutyrophenone, m. p. 218°, was also synthesised by condensing benzaldehyde with the nitrile (I) in presence of potassium methoxide. The action of magnesium methoxide on methyl 3-cyano-2-benzoyl-1-phenyl*cyclo*propane-3-carboxylate (A., 1923, i, 54) afforded *methyl* α-*cyano*-β-*benzoyl*-γ-*phenyl*-Δ^{β}-*butenoate*, $CHPh{:}C(COPh)\cdot CH(CN)\cdot CO_2Me$, prisms, m. p. 104°. F. G. W.

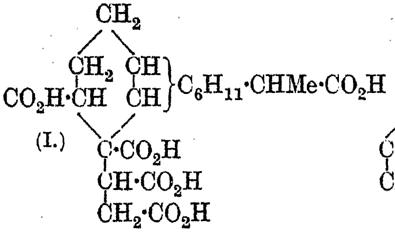
Study of the Freezing of Solutions as a Method of Investigating some problems in Pure Chemistry. I. Systems containing *sec.*-Butyl Alcohol and its Derivatives. R. H. Lombaers (*Bull. Soc. chim. Belg.*, 1924, **33**, 232—245).—The system phthalic anhydride–*sec.*-butyl alcohol gives a normal freezing-point curve provided that the system is not subjected to prolonged heating at temperatures above 110°; under the latter conditions, the phthalate is formed in equilibrium with its components. This reaction is considered to be reversible, since the products of dissociation can be extracted from the fused phthalate. The equilibrium conditions between the phthalate and each of its components in excess were studied separately. With the anhydride, a normal curve indicating a eutectic at 53·6° (95 mols. anhydride, 5 mols. phthalate) was observed; with the alcohol, the eutectic could not be detected, and no evidence of the formation of a neutral phthalate was obtained. The freezing-point curves of mixtures of the racemic and active forms of the phthalate are of a type not hitherto observed. F. B.

Potassium Salts of Phenolphthalein. H. Bassett and D. J. T. Bagnall (*J. Chem. Soc.*, 1924, **125**, 1366—1373).—The system phenolphthalein–potassium hydroxide–water at 25° gives results rather less definite than those obtained with the sodium compounds (T., 1923, **123**, 1291), the curves corresponding with the hydrates of the mono-, di-, and tri-potassium salts being practically continuous. The mono-potassium salt gave hydrates with 5, 4, and 3 mols. of water; the di-salt with 10, 9, and 8 mols., and the tri-salt with 9, 8, 7, 6, 5, and 4 mols. of water. The tripotassium salt as tetrahydrate can exist in contact with a range of solutions in which the ratio potash : phenolphthalein is less than that for the tri-salt and also with solutions supersaturated with respect to $KOH,2H_2O$ (cf. Pickering, T., 1893, **63**, 890). No red salt was obtained as a solid phase, but dehydration experiments indicated that a red salt of phenolphthalein can exist in the solid state. By heating the dry tripotassium salt to constant weight at 150° a deep red product was obtained corresponding in composition with a dihydrate of the tripotassium salt. It is probably either the dipotassium salt, $CO_2K\cdot C_6H_4\cdot C(C_6H_4\cdot OK){:}C_6H_4{:}O$ (formed by elimination of potassium hydroxide) or an equimolecular mixture of the mono-salt, $CO_2K\cdot C_6H_4C(C_6H_4\cdot OH){:}C_6H_4{:}O$, and a hydrate, $2KOH,H_2O$. The colour of the red dehydration product is unaltered on heating at 100° in a current of dry carbon dioxide, but in contact with the mother-liquors from the tripotassium salt the red colour disappears. The dry, colourless monopotassium salt partly melts in its water of crystallisation at 100°, giving a deep red, viscous mass, whilst on treatment with water it gives a red solution and a precipitate of phenolphthalein. R. B.

Bile Acids. XX. Conversion to a Tricarboxylic Acid. H. Wieland and O. Schlichting (*Z. physiol. Chem.*, 1924, **134**, 276—289; cf. A., 1921, i, 346; 1922, i, 41).—The second reaction product already described as resulting, together with norsolanellic acid, from the oxidation of pyrodeoxybilianic acid with fuming nitric acid proves to be a *tetracarboxylic acid*, $C_{16}H_{24}O_8$. It is prepared more conveniently by the action of fuming nitric and sulphuric acids on the diketo acid, $C_{23}H_{34}O_6$, obtained from pyrodeoxybilianic acid by oxidation with permanganate. It has m. p. 218° (decomp.). Its *methyl* ester, formed by the action of diazomethane, has b. p. 200—207°/0·3 mm. The acid on heating gives a monoketodicarboxylic *pyro acid*, $C_{15}H_{22}O_5$, m. p. 187°; this is oxidised by nitric acid to an optically active *tricarboxylic acid*, $C_{13}H_{20}O_6$, m. p. 187°, with slight sintering; on heating, it gives an *anhydride*, $C_{13}H_{18}O_5$, m. p. 147—148°. For the interpretation of these results in relation to the structure of the bile acid molecule, the original paper must be consulted.

C. R. H.

Bile Acids. XVIII. Chollepidanic Acid. H. Wieland [with B. Flaschenträger and A. Rewolle] (*Z. physiol. Chem.*, 1924, **134**, 140—148).—When deoxybilianic acid (20 g.) is heated for 2 hours with 100 c.c. of fuming nitric acid (*d* 1·52), there is formed, along with choloidanic acid and two other acids, chollepidanic acid, $C_{21}H_{30}O_{10}$ (cf. Wieland, A., 1921, i, 113). The yield of the purified acid is about 25% of the deoxybilianic acid used. It blackens and decomposes but does not melt at 280°. To this acid formula (I) is assigned. The *pentamethyl* ester, $C_{21}H_{25}O_5(OMe)_5$, glistening needles arranged in rosettes, m. p. 102°, is formed from the silver salt and methyl iodide. The *monomethyl* ester, m. p. 275°, is formed when hydrogen chloride is passed into a boiling alcoholic solution of the acid. When chollepidanic acid is heated in a vacuum, the tribasic *pyrochollepidanic acid*, $C_{20}H_{28}O_7$, m. p. 266°, is obtained, and to it is assigned formula (II). This acid may be oxidised by potassium permanganate in alkaline solution to a tetrabasic *acid*, $C_{19}H_{28}O_9$, m. p. 234°, with the probable constitution (III).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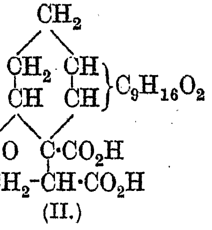
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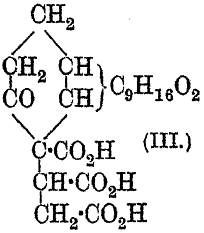
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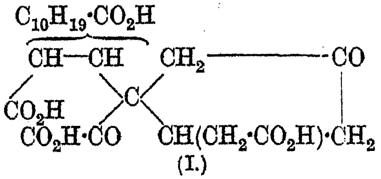
W. O. K.

Bile Acids. XIX. Further Oxidation of Pyrodeoxybilianic Acid. H. Wieland and W. Mothes (*Z. physiol. Chem.*, 1924, **134**, 149—157).—When the diketotetracarboxylic acid, $C_{23}H_{34}O_6$, obtained from pyrodeoxybilianic acid by oxidation (A., 1921, i, 112) is further oxidised at 66° with potassium permanganate, *norcilianic acid*, $C_{23}H_{32}O_{10}$, a tetrabasic acid, m. p. 122° (decomp.), and *isonorcilianic* acid, isolated as the *sodium* salt, $C_{23}H_{31}O_{10}Na$, are obtained. To these acids are assigned formulæ (I) and (II), respectively. On further oxidation with chromic acid, both yield biloidanic acid. Norcilianic acid forms a *semicarbazide* of the *semicarbazone*, $C_{25}H_{38}O_{10}N_6$, and when methylated with diazomethane yields a *pentamethyl* ester, m. p. 138—139°.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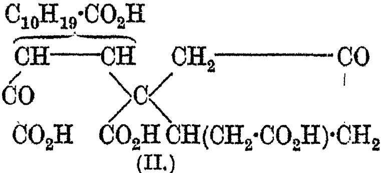
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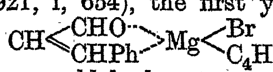
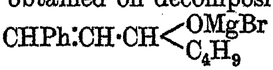
W. O. K.

Mechanism of Phenylhydrazone Formation. S. Bodforss (*Z. physikal. Chem.*, 1924, **109**, 223—259).—The reactions between phenylhydrazine and ketones and aldehydes have been studied kinetically. The conductivity method proving unsuitable, the reaction was followed by titrating the phenylhydrazine with silver nitrate. It is found that the velocity of the reactions with *m*-nitrobenzaldehyde and other aromatic aldehydes is determined by the rate of decomposition of an intermediate compound. With aldehyde in excess, the reaction gives a unimolecular constant. With hydrazine in excess, the results are complex. The reaction with acetophenone is bimolecular in presence of excess of ketone, and probably unimolecular with excess of phenylhydrazine. S. B.

Polymorphic Nitrobenzaldehydehydrazones. F. D. Chattaway and A. J. Walker (*J. Chem. Soc.*, 1924, **125**, 1207—1215).—*o*-Nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone, *p*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone, and *p*-nitrobenzaldehyde-4-chloro-2-bromophenylhydrazone exist in two well-defined forms, a yellow or orange, labile form, separating first, and a dark red, stable form into which the labile is transformed in contact with a solvent. *p*-Nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone is trimorphic, the least stable, yellow, hair-like, non-pleochroic needles changing into orange, monoclinic needles and these into dark red, orthorhombic crystals, the transition temperature of the latter change being about 154°. The solubility curves of the labile and stable forms of these hydrazones in alcohol are practically parallel and the solubility ratios, labile : stable, are exceptionally large. The rates of transformation of the labile forms in contact with different solvents were determined approximately and crystallographic measurements of the stable forms were made. The stable forms of the three *p*-nitrobenzaldehyde-2 : 4-dihalogenophenylhydrazones crystallise in the orthorhombic system, and those of *o*-nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone and *p*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone (of which only one form was observed) in the monoclinic system. R. B.

Compounds of Magnesium Alkyl Halides with Carbonyl Compounds and the Reducing Action of Grignard Reagents. II. K. Hess and W. Wustrow (*Annalen*, 1924, **437**, 256—273; cf. A., 1921, i, 777).—The reducing action of magnesium alkyl halides previously observed in the case of benzaldehyde (cf. also Leroid, A., 1922, i, 215) has now been studied with the unsaturated aldehydes crotonaldehyde and cinnamaldehyde, and in both cases the unsaturated alcohol was obtained. Cinnamaldehyde and magnesium *iso*butyl halides form at low temperatures bright yellow, stable additive compounds of 1 mol. of aldehyde and 1 mol. of Grignard reagent, which on decomposition with water yield α-phenyl-ε-methyl-Δ^{α}-hexen-γ-ol. On warming, the additive compound decomposes, giving *iso*butylene and a colourless compound, which on decomposition with water yields cinnamaldehyde. These changes are represented by co-ordination formulæ of the type previously suggested. If the co-ordination number 4 is assumed for magnesium (cf. Meisenheimer and Casper, A., 1921, i, 654), the first yellow compound (I) must be represented by  $CH{<}{\begin{smallmatrix}CHO\cdots\\ CHPh\cdots\end{smallmatrix}}{>}Mg{<}{\begin{smallmatrix}Br\\ C_4H_9\end{smallmatrix}}$ but the corresponding substituted hydrocinnamaldehyde,

$$CHPh(C_4H_9)\cdot CH_2\cdot CHO,$$

has not been obtained on decomposition with water. An isomeric compound,  $CHPh{:}CH\cdot CH{<}{\begin{smallmatrix}OMgBr\\ C_4H_9\end{smallmatrix}}$ (III), has been obtained by the action of magnesium ethyl bromide on α-phenyl-ε-methyl-Δ^{α}-hexen-γ-ol; on warming, this yields no butylene, but reacts with water, forming the secondary alcohol, $CHPh{:}CH{\cdot}CH(C_4H_9){\cdot}OH$, or its anhydro product, α-phenyl-ε-methyl-$\Delta^{\alpha\gamma}$-hexadiene. The two isomerides are also distinguished by their behaviour with acetyl chloride, the first leading to cinnamaldehyde and the second to α-phenyl-ε-methyl-Δ^{α}-hexen-γ-yl acetate. The colourless compound, $CHPh{:}CH{\cdot}CH_2{\cdot}O{\cdot}MgBr$ (II), on treatment with acetyl chloride, yields cinnamyl acetate, but no cinnamaldehyde.

The action of magnesium ethyl bromide on crotonaldehyde yields only Δ^{β}-hexen-δ-ol (Rief, A., 1906, i, 394). Magnesium sec.-*n*-butyl bromide yields chiefly *ε-methyl-Δ^{β}-hepten-δ-ol*, a mobile oil, b. p. 69—70°/18 mm., α_4^{20} 0·8473, n_D^{20} 1·44113, besides a little crotyl alcohol (*α-naphthylurethane*, long needles, m. p. 89°) and a little dicrotyl ether. Better yields of crotyl alcohol were obtained with magnesium *iso*butyl bromide and using phenetole in place of ether, *iso*butylene being also formed. The following constants of crotyl alcohol are given: b. p. 118°/764 mm., d_4^{20} 0·8539, n_α^{20} 1·41898, n_D^{20} 1·42403, n_β^{20} 1·43156, n_γ^{20} 1·43705. Magnesium *cyclo*hexyl chloride gives only α-cyclo*hexylbuten-α-ol*, a colourless oil of aromatic odour, b. p. 98—100°/13 mm., $d_4^{14.5}$ 0·9225, n_α^{20} 1·47623, n_D^{20} 1·47987, n_β^{20} 1·48635, n_γ^{20} 1·49245.

Magnesium ethyl bromide and cinnamaldehyde yield the bright yellow additive *compound*, $CHPh{:}CH{\cdot}CHO,MgBrEt$, which with water yields α-phenyl-Δ^{α}-penten-γ-ol (Klages, A., 1906, i, 661) for which constants are given, and on heating with methyl alcohol loses ethylene, giving a *compound*, C_9H_9OBrMg, from which only resinous products were obtained. The analogous *additive* compound, $CHPh{:}CH{\cdot}CHO,MgBrC_4H_9$, obtained from magnesium *iso*butyl bromide or chloride at −10°, contains 1 mol. of ether which is only partly lost on drying. With ammonium chloride solution in the cold, it yields *α-phenyl-ε-methyl-Δ^{α}-hexen-γ-ol*, thin needles, m. p. 37°, b. p. 160—162°/15 mm. (*benzoate*, m. p. 59—60°). On boiling with methyl alcohol, the additive compound loses butylene, yielding a compound, $CHPh{:}CH{\cdot}CH_2{\cdot}OMgBr$, from which only resinous products could be obtained. If, however, the decomposition takes place in boiling ether, the product obtained has the same composition, but yields cinnamyl alcohol (p-*nitrobenzoate*, m. p. 74—75°), on treatment with water, and on treatment with acetyl chloride *cinnamyl acetate*, b. p. 140—141°/18 mm., d_4^{12} 1·0567, n_α^{12} 1·5369, n_D^{12} 1·54415, n_β^{12} 1·55915, n_γ^{12} 1·57267, and α-phenyl-ε-methyl-$\Delta^{\alpha\gamma}$-hexadiene. The additive *compound*, $CHPh{:}CH{\cdot}CHO,MgClC_4H_9$, from magnesium *iso*butyl chloride and cinnamaldehyde on treatment with acetyl chloride, yields cinnamyl acetate and α-phenyl-ε-methyl-$\Delta^{\alpha\gamma}$-hexadiene, whilst the compound obtained from magnesium ethyl bromide and α-phenyl-ε-methyl-Δ^{α}-hexen-γ-ol yields only the corresponding acetate and α-phenyl-ε-methyl-$\Delta^{\alpha\gamma}$-hexadiene. R. B.

Simplification of the Gattermann Synthesis of Aromatic Aldehydes. II. R. ADAMS and E. MONTGOMERY (*J. Amer. Chem. Soc.*, 1924, **46**, 1518—1521; cf. this vol., i, 51).—Aldehydo derivatives of phenols and phenol ethers may be prepared in good yields by saturating a cooled mixture of the phenol or phenol ether (1 mol.), powdered zinc cyanide (2 mols.), and benzene, with hydrogen chloride, adding powdered anhydrous aluminium chloride, and then passing in a slow stream of hydrogen chloride at 40—45° for 3—4 hours. The imine hydrochloride is precipitated by addition of excess of 10% hydrochloric acid, and hydrolysed to the aldehyde by refluxing. F. G. W.

Mobility of Organically Combined Chlorine in the Friedel-Crafts Reaction. Influence of the Solvent. CHOPIN (*Bull. Soc. chim.*, 1924, [iv], **35**, 610—614).—The rates of reaction between acetyl chloride and benzene in the following solvents decrease in the order benzene, light petroleum, chlorobenzene, bromobenzene, carbon disulphide, nitrobenzene, the reaction being carried out at 4° under reduced pressure, and its progress followed by determination of the hydrogen chloride liberated. In nitrobenzene, the reaction is much slower if the aluminium chloride is dissolved prior to the addition of the other reactants. Chromium chloride in chlorobenzene gave practically no reaction, whilst with ferric chloride the above temperature is too low. Naphthalene reacts more slowly, toluene more rapidly, than benzene. In the reaction between acetyl chloride and naphthalene, the product in light petroleum solution is a mixture of about equal parts of α- and β-naphthyl methyl ketones. In nitrobenzene, the β- predominates; in bromobenzene, the α- predominates, and is formed exclusively in chlorobenzene and carbon disulphide. F. G. W.

The Beckmann Rearrangement. A. LACHMAN (*J. Amer. Chem. Soc.*, 1924, **46**, 1477—1483).—Benzophenoneoxime decomposes when heated at 185°, either alone or in presence of sodium or potassium chloride (cf. Hantzsch and Kraft, A., 1892, 338) with formation of benzophenone and benzophenoneimine in approximately equimolecular proportions, nitrogen, oxides of nitrogen, and water. The latter hydrolyses some of the benzophenoneimine, yielding ammonia in amount corresponding exactly with the excess of benzophenone found in the reaction product. No benzanilide is formed, and the reaction forms a convenient method of preparing benzophenoneimine. Lehmann's observations (*Z. angew. Chem.*, 1923, **36**, 360) on the decomposition of benzophenoneoxime in presence of hydrogen chloride were verified, but the formation of benzanilide by less than one equivalent of hydrogen chloride at slightly higher temperatures, and even in presence of water, was demonstrated. It is concluded that the Beckmann rearrangement is the direct conversion of the oxime salt into the acid amide and free acid, according to the equation $CPh_2{:}NOH,HCl=COPh{\cdot}NHPh+HCl$. Pure benzophenoneoxime, of which a convenient method of preparation is described, has m. p. 143°. F. G. W.

Preparation of Anthraquinone Derivatives. H. A. E. DRESCHER, J. THOMAS, and SCOTTISH DYES, LTD. (Brit. Pat. 214765). —Imidoanthraquinones are obtained by treating a halogen derivative of anthraquinone with the imide of a dibasic acid (*e.g.*, phthalimide) or a metallic salt of the imide in the presence of metallic copper (*e.g.*, copper bronze) or a copper salt. The imidoanthraquinones are converted into aminoanthraquinones by hydrolysis, *e.g.*, with concentrated sulphuric acid. Substituted benzoylamidoanthraquinones are prepared by partial hydrolysis of phthalimidoanthraquinones, *e.g.*, with boiling, dilute sodium hydroxide.

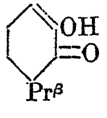
Details are given of the preparation of 1-*phthalimido*-, 2-*phthalimido*-, 1 : 5-*diphthalimido*-, 1-*chloro*-5-*phthalimido*-, 2-*nitro*-1-*phthalimido*-, 1-*amino*-4-*phthalimido*-2-*methyl*-, 1-*methylamino*-4-*phthalimido*-, and 2-amino-1-phthalimido-anthraquinones, and of their conversion into the corresponding aminoanthraquinones; also of the preparation of 2-benzoylamidoanthraquinone-2′-carboxylic acid by partial hydrolysis of 2-phthalimidoanthraquinone.

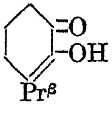
W. T. K. B.

Terpenes and Ethereal Oils. CXXVII. Diosphenol (Buchu-camphor) and Homologous Compounds. O. WALLACH and A. WEISSENBORN (*Annalen*, 1924, **437**, 148—186; cf. A., 1916, i, 487; 1918, i, 440, 442).—Both dibromomenthone and dibromocarvomenthone yield, on treatment with alkali, the same product, diosphenol (buchu-camphor), and on treatment with ammonia in methyl-alcoholic solution give two isomeric monobrominated amines, which are stable in acid solution but in the presence of sodium hydroxide are both converted into diosphenol, with evolution of ammonia. If the ammonia is replaced by piperidine or other amines, stable, well-crystallised monobrominated bases can be isolated. In both cases, the tertiary bromine atom is the more mobile and the first step in the reaction is replacement of the bromine atom by an amine residue and not splitting off of hydrogen bromide. A mechanism is suggested to explain the conversion of both menthone and carvomenthone derivatives into diosphenol.

The structure of diosphenol has been established as 2-hydroxy-Δ^1-menthen-3-one (I), by its synthesis by oxidation of Δ^1-menthen-3-one through the 1 : 2-dihydroxyketone; carvenone (Δ^3-menthen-2-one) under similar conditions yields the isomeric form (II). The *o*-*cyclo*hexandiones do not appear to be capable of existence except under special conditions. The general name, diosphenols, is proposed for the homologous series of 1 : 2-hydroxy*cyclo*hexenones. They possess reducing properties, and give well crystallised dioximes derived from the *o*-diketones. These dioximes give complex compounds with the metals of the eighth group; the nickel compounds are characterised by their insolubility and intense

(I.)





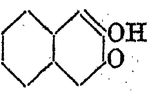
(II.)

red or orange colour, and can be applied in the detection or determination of nickel. A dicyclic diosphenol obtained from β-ketodecahydronaphthalene by analogous methods possesses similar properties to the monocyclic diosphenols. On heating with potassium hydroxide the bicyclic diosphenol is converted into an α-hydroxy acid which on oxidation yields hydrindone, the six-membered ring being converted into a five-membered, as previously observed in the *cyclo*hexanone series (A., 1918, i, 442; 1919, i, 267).

The conversion of 2 : 4-dibromomenthone into diosphenol is most easily accomplished by treatment with ammonia in alcoholic solution, the brominated amine (syrupy hydrochloride) being more easily decomposed with sodium hydroxide than the *piperidide*, $C_{15}H_{26}ONBr$, needles or prisms, m. p. 127—128°, or *anilide*, $C_{16}H_{22}ONBr$, needles, (decomp.) 180°. Similarly, dibromocarvomenthone (1 : 3-dibromomenthan-2-one) yields a *bromopiperidide*, $C_{15}H_{26}ONBr$, m. p. 115—116°. Both the active and inactive preparations yield inactive diosphenol. With sodium methoxide, inactive 1 : 3-dibromomenthan-2-one is converted into 3-*bromo*-1-*hydroxymenthan*-2-*one*, m. p. 92° (*acetyl* derivative, m. p. 155°), which is converted into diosphenol by treatment with alkali.

Oxidation of Δ^1-menthen-3-one with cold dilute potassium permanganate in acetone solution yields diosphenol, m. p. 83° (phenylurethane, m. p. 113—114°; cf. Asahina and Mituhori, A., 1922, i, 667). Carvenone under similar conditions gives an *oil* yielding the diosphenol reaction with ferric chloride. It dissolves in sodium hydroxide and, on acidifying, the diosphenol, m. p. 83°, separates. Both diosphenols yield the same dioxime, but the liquid diosphenol yields a *phenylurethane*, $C_{17}H_{21}O_3+H_2O$, m. p. 165—166°.

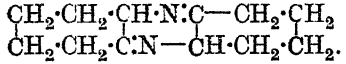
β-Ketodecahydronaphthalene (dibenzylidene derivative, m. p. 119—120°; α-ketotetrahydronaphthalene gives a *monobenzylidine* derivative, m. p. 206—207°) on bromination in acetic acid yields a viscous fluid which on shaking with 20% potassium hydroxide yields a dibasic *acid*, $C_{10}N_{16}O_4$, m. p. 165° (together with a lower melting acid, cf. Hückel, this vol., i, 31), and the *diosphenol*, $C_{10}H_{14}O_2$ (annexed formula), colourless, rhombic crystals, m. p. 88—89°. The *dioxime*, m. p. 196—197°, gives an intense bright orange precipitate with nickel salts. Besides the diosphenol, a small quantity of an isomeric *substance*, m. p. 99—100°, is formed, yielding a very insoluble deep red *dioxime*. On heating with potassium hydroxide at 120—130°, the diosphenol, m. p. 88—89°, yields a mixture of two acids difficult to separate. The more readily purified product is an α-*hydroxy acid*, $C_{10}H_{16}O_3$, m. p. 128—129°, which on oxidation with lead peroxide and sulphuric acid yields hexahydro-2-hydrindone, $C_9H_{14}O$ (semicarbazone, m. p. 240°; cf. Borsche and Lange, this vol., i, 33; *oxime*, m.p. 160—161°), a result which points to a ββ-structure for the diosphenol of m. p. 88—89°. The second *acid*, $C_{10}H_{16}O_3$, m. p. about 100°, on oxidation yields a mixture of ketones which give a semicarbazone with melting point



approximating to that of the semicarbazone of hexahydro-1-hydrindone.

The *monoxime* of buchu-camphor, m. p. 124° (cf. Kondakov, A., 1897, i, 227; Semmler, A., 1906, i, 373), gives a yellow solution in alkali, whereas the *dioxime*, m. p. 197°, gives a nearly colourless solution. The monoxime is stable in acid solution, but when the dioxime is boiled with dilute acid, diosphenol is partly regenerated. The dioxime gives a very insoluble orange *nickel* compound.

The simplest diosphenol, *2-hydroxy-*Δ^1-cyclo*hexen-3-one*, m. p. 38—40°, b. p. 193—195° (*phenylurethane*, m. p. 124°), was obtained from dibromo*cyclo*hexanone, m. p. 106—107°, by the action of potassium hydroxide. Concentrated potassium hydroxide converts it into 1-hydroxy*cyclo*pentane-1-carboxylic acid. With phenylhydrazine, it yields an osazone, golden-yellow needles, m. p. 152—153°, identical with that obtained from 1-hydroxy*cyclo*hexan-2-one; the *dioxime* has m. p. 189—190°, yields a *dibenzoyl* compound, m. p. about 170° (decomp.), and an intense red *nickel* compound, $C_{12}H_{18}O_4N_4Ni$, which can be used for the determination of nickel. On reduction with zinc dust and potassium hydroxide, the dioxime yields a colourless *base*, $(C_6H_9N)_2$, m. p. 108—109° (insoluble *picrate*), which is probably a phenazine of the structure



$$\begin{array}{l}CH_2\cdot CH_2\cdot CH\cdot N{:}C-CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot C{:}N-CH\cdot CH_2\cdot CH_2.\end{array}$$

2-Hydroxy-Δ^1-*cyclo*hexen-3-one can also be obtained by converting Δ^1-*cyclo*hexenone into the ketoglycol, $C_6H_6(OH)_2O$, and treating this with dilute sulphuric acid or by careful oxidation of 1-hydroxy*cyclo*hexan-2-one, whilst the formation of its dioxime can be easily detected when hydroxylamine acts on the product obtained by the action of nitrous acid on *cyclo*hexanone (cf. Borsche, A., 1910, i, 178).

1 : 3-Dibromo-1-methyl*cyclo*hexan-2-one is converted by potassium hydroxide into 2-hydroxy-1-methyl-Δ^1-*cyclo*hexen-3-one, m. p. 63° (diphenylhydrazone, m. p. 150—151°, *dioxime*, m. p. 165—166°, yielding an orange *nickel* compound), which yields two semicarbazones, one, needles, m. p. 174—175°, and a more insoluble isomeride, m. p. 240°. The diosphenol is identical with the product obtained by Harries from 1-methyl-Δ^1-*cyclo*hexen-3-one (A., 1902, i, 378). The *bromopiperidide*, $C_{12}H_{20}ONBr$, has m. p. 110—111°. Similarly, the dibromo-derivative of 4-methyl*cyclo*hexanone yields an oily diosphenol which with hydroxylamine gives 1-*methyl*cyclo*hexan-3 : 4-dione dioxime*, needles, m. p. 180—181° (decomp.) [*dibenzoyl* derivative, m. p. about 170° (decomp.), deep red *nickel* compound, very insoluble]. The same diosphenol and dioxime were obtained similarly from 3-methyl*cyclo*hexanone, a small quantity of 1-methyl*cyclo*hexan-2 : 3-dione dioxime being also isolated, indicating the formation of the 2 : 3-dione as a by-product. The diosphenol, $C_8H_{12}O_2$, m. p. 71—72°, obtained previously (A., 1918, i, 442) from 1 : 3-dimethyl*cyclo*hexan-5-one is identical with the product prepared from 1 : 5-dimethyl-Δ^1-*cyclo*hexen-3-one and must be regarded as 2-hydroxy-1 : 5-dimethyl*cyclo*hexen-3-one

(*dioxime*, m. p. 163—164°, orange *nickel* compound). The diosphenol, $C_9H_{14}O_2$, m. p. 90°, prepared from dibromodihydro*iso*phorone (A., 1916, i, 487) is identical with the product obtained by oxidation of *iso*phorone (1 : 5 : 5-trimethyl-Δ^1-*cyclo*hexen-3-one) and must therefore be 2-hydroxy-1 : 5 : 5-trimethyl*cyclo*hexan-3-one (*dioxime*, m. p. 177—178°, orange-yellow *nickel* compound). R. B.

New Form of Fenchoneoxime. Characterisation of Fenchone in presence of Camphor. M. Delépine (*Compt. rend.*, 1924, **178**, 1721—1723).—When *d*-fenchone was treated with hydroxylamine in alkaline solution according to Rimini's method (A., 1896, i, 359), it gave, not the expected α-oxime (m. p. 165°, $[\alpha]_D+47°$), but a much more soluble compound, β-*fenchoneoxime*, m. p. 123°, $[\alpha]_D+129{\cdot}3°$. This is converted into the usual α-form by being heated alone at 170—180°, or by evaporating its alcoholic solution to dryness, or by boiling an acidified alcoholic solution, or even if the solution is kept for some time. The reverse change, α into β, was not effected; although the formation of the β-variety evidently depended on the alkalinity of the mother-liquor, yet treatment of the α-form with alcoholic alkali hydroxide brought about no conversion. The two forms ($[\alpha]_D-96°$, and $[\alpha]_D-47°$, respectively) were also obtained from *l*-fenchone (cf. Wallach, A., 1893, i, 105).

A mixture of camphor and fenchone can be treated and so the proportion of fenchone determined. The oximes are separated by fractional crystallisation, taking advantage of the readier solubility of camphoroxime in alkaline media. W. A. S.

Reduction of Glycidic Esters in the Terpene Series. Synthesis of Inactive Citronellol and Rhodinol. A. Verley (*Bull. Soc. chim.*, 1924, [iv], **35**, 608—610).—Inactive citronellol and inactive rhodinol are obtained, respectively, by the reduction, with sodium and amyl alcohol, of the glycidic esters of α- and β-methylheptenones. Behal's failure to repeat the author's synthesis of nerol, and the action of ozone on methylheptenone are discussed. F. G. W.

Formation and Catalytic Decomposition of Terpinolene. A. Mailhe (*J. Usines Gaz*, 1923, **47**, 370—373).—Terpin, when passed over alumina in glass at 310—320°, yields terpinolene; terpineol yields a liquid, presumably terpinolene. The catalyst remains active for several days, and is easily regenerated by heat. Terpinolene passed over copper turnings at 500—550° gave a gas containing 27% C_nH_{2n}, 15% C_nH_{2n+2}, 18% CH_4, 40% H_2, and a liquid containing benzene, *cyclo*hexane, toluene, methyl*cyclo*hexane, *m*-xylene, and *m*-cymene. Chemical Abstracts.

Abnormal Phenomena in the Terpene Group in the Light of an Extension of Thiele's Hypothesis. K. Sławiński (*Roczniki Chemji*, 1923, **3**, 200—204).—Pinene and camphene behave abnormally on oxidation and addition of halogen acids in that some derivatives are formed by the addition, for example, of the elements of water and oxygen to the double bond (formation of corresponding glycols) whilst others are due to the fission of the bridge (formation of bornyl chloride, sobrerol, etc.). It is suggested that these phenomena can be accounted for by assuming that the system formed by a ring conjugated with a double linking, such as is present in vinyltrimethylene, camphene, and pinene, behaves like a pair of conjugated double linkings towards oxidising and other agents (cf. Eisenlohr, *Spectrochemie der organischen Verbindungen*, 1912). G. A. R. K.

Essential Oil of *Pinus pinea*. G. Dupont and M. Barraud (*Bull. Soc. chim.*, 1924, [iv], **35**, 625—631).—The essential oil of *Pinus pinea* consists of *l*-limonene (75·4%) of greater optical activity ($[\alpha]_D$ −123·7°) than any natural limonene previously obtained, together with pinene (16·7%) and an inactive sesquiterpene, d^{15} 0·9157, n_D^{20} 1·4983 (6·6%). [Cf. *B.*, 1924, 615.] F. G. W.

New Synthetic Nitrophenol Glucosides and the Disinfectant Action and Toxicity of the Nitrophenols. E. Glaser and W. Wulwek.—(See i, 797.)

The Properties of Loroglossin and its Products of Hydrolysis, Dextrose and Loroglossigenin. M. Bridel and P. Delauney (*J. Pharm. Chim.*, 1924, [vii], **29**, 393—402; cf. A., 1919, i, 243).—Loroglossin, $C_{30}H_{42}O_{18}$, is an odourless and bitter glucoside which has been extracted from sixteen species of the order *Orchidaceæ* in the form of long, colourless needles, having no sharp m. p. (about 140—150°). The anhydrous substance gives $[\alpha]_D$ −45·65° in water, and −36·28° in 50% methyl-alcoholic solution. Its aqueous solution froths strongly when shaken. It gives a red colour with cold, concentrated sulphuric acid, but no coloration with cold nitric acid, hydrochloric acid, or ferric chloride. It is hydrolysed by sulphuric acid, giving 51·41% of dextrose and a substance, *loroglossigenin*, crystals, m. p. 77°, having an odour of mown hay. The substance is best obtained by the hydrolysis of loroglossin with emulsin, although the reaction proceeds slowly. It behaves like loroglossin towards sulphuric acid, but gives with ferric chloride a faint violet coloration, which disappears on shaking with ether or on warming. It has no reducing properties.

W. T. K. B.

Synthesis of Amygdalin. R. Campbell and W. N. Haworth (*J. Chem. Soc.*, 1924, **125**, 1337—1343; cf. Haworth and Wylam, T., 1923, **123**, 3120).—Ethyl *dl*-mandelate condenses with β-bromohepta-acetylgentiobiose in the presence of silver oxide, giving ethyl *dl*-hepta-acetylamygdalinate, m. p. 205°, $[\alpha]_D$ −62·0° (cf. Zemplén, this vol., i, 617). The same product was obtained by acetylation of *dl*-amygdalinic acid and crystallisation of the hepta-acetylamygdalinic acid from alcohol, when direct esterification takes place, and by methylation of silver amygdalinate with methyl iodide followed by acetylation of the ester with acetic anhydride and sodium acetate, a by-product, m. p. 184—186°, $[\alpha]_D$ −28·6°, being obtained on one occasion. On treatment with ammonia in dry methyl alcohol, ethyl *dl*-hepta-acetylamygdalinate is converted into *dl*-amygdalinamide, a colourless, brittle solid, $[\alpha]_D$ −77·0°, which on acetylation in the presence of pyridine yielded *hepta-acetylamygdalinamide* in two isomeric forms, m. p. 166—167° and 152 153°, and $[\alpha]_D$ −68·6° and −49·7°, each containing 1 mol. of combined pyridine, which were separated by crystallisation from alcohol. The acetylated amide, m. p. 166—167°, on digestion with phosphoric oxide in xylene solution, yielded *d*-hepta-acetylamygdalin, $[\alpha]_D$ −36·2° (Caldwell and Courtauld, T., 1907, **91**, 671), the de-acetylation of which has already been effected by Fischer and Bergmann (A., 1917, i, 657). R. B.

Strophanthin. IV. Anhydrostrophanthidin and Dianhydrostrophanthidin. W. A. Jacobs and A. M. Collins (*J. Biol. Chem.*, 1924, **59**, 713—730; cf. A., 1923, i, 123; this vol., i, 65).—The action of 10% absolute alcoholic hydrochloric acid on strophanthidin at room temperature gives a product, $C_{25}H_{34}O_5$, which is characterised as the *ethylal* of *oxidoanhydrostrophanthidin*, needles, m. p. 223—230°; $[\alpha]_D$ −50°. On alkaline hydrolysis this gives an *acid*, $C_{25}H_{36}O_6$, rhombic plates, m. p. 120—125° (decomp.); *methyl* ester, m. p. 182—186°; $[\alpha]_D^{25}$ −81·7° in chloroform; on acid hydrolysis it gives anhydrostrophanthidin. If strophanthidin be boiled with 5% alcoholic hydrogen chloride 2 mols. of water are eliminated and the ethylal of oxidodianhydrostrophanthidin is formed, which, in turn, on acid hydrolysis gives dianhydrostrophanthidin, $C_{23}H_{28}O_4$. Both anhydro- and dianhydro-strophanthidin form an oxime, a phenylhydrazone, a monoacetate, and a monobenzoate. The substance, $C_{24}H_{30}O_4$, previously described by Windaus and Hermanns (A., 1915, i, 704) as anhydrostrophanthidin, has been identified as the methylal of oxidodianhydrostrophanthidin. A similar series of reactions has been carried through with dihydrostrophanthidin. The dianhydro derivatives both of strophanthidin and of dihydrostrophanthidin exhibit mutarotation.

It is concluded that the molecule of strophanthidin contains three hydroxyl groups, a carbonyl group and a lactone group. The formula of the basic hydrocarbon skeleton of strophanthidin becomes $C_{23}H_{40}$ and indicates the probable relationship of this substance to cholesterol and the bile acids.

Anhydrostrophanthidin, $C_{23}H_{30}O_5$, forms needles with $2H_2O$ from 50% alcohol; m. p. (air-dried) 223—226°, with slight sintering; $[\alpha]_D^{t}$ −145° in 95% alcohol; *oxime*, small prisms with $1H_2O$ from 95% alcohol; m. p. 260—265°; *phenylhydrazone*, needles containing $2H_2O$, m. p. (air-dry) 260—264°. The *acetate*, clusters of needles, sinters at 280° and melts at 292—294°. The *benzoate*, flat needles and platelets, sinters at 270° and melts at 287—289°.

The *ethylal* of *dianhydrostrophanthidin*, $C_{25}H_{32}O_4$, forms colourless needles which on rapid heating sinter at 238° and melt at 249—251°; $[\alpha]_D^{23}$ $-142°$ in chloroform. The *acid*, $C_{25}H_{34}O_5$, obtained by alkaline hydrolysis of the above, forms needles, m. p. 198—200° (decomp.), $[\alpha]_D^{26}$ $-85{\cdot}5°$ in chloroform; *methyl* ester, colourless needles, m. p. 152—156°. The *methylal* of *dianhydrostrophanthidin*, $C_{24}H_{30}O_4$, forms long needles sintering at 245°, m. p. 252—254°; $[\alpha]_D^{24}$ $-131°$ in chloroform.

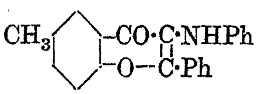
Dianhydrostrophanthidin, $C_{23}H_{28}O_4$, forms needles, m. p. 233—236°; $[\alpha]_D^{4}$ $-222°$ in chloroform; *oxime*, stout prisms, m. p. 279—281° with effervescence, $[\alpha]_D^{25}$ $-174°$ in pyridine; *phenylhydrazone*, needles or platelets containing $1{\cdot}5H_2O$, m. p. (air-dry) 219—227°, $[\alpha]_D^{25}$ $-245°$ in chloroform. The *acetate*, stout prisms with $0{\cdot}5H_2O$, softens at 180° to a resin which melts at 203—206°, $[\alpha]_D^{22}$ $-222°$ in chloroform. The *oxime* of the acetate forms platelets, m. p. 224—226°; the *oxime* of the *benzoate*, prisms, m. p. 283—285°.

The *ethylal* of *oxidodianhydrodihydrostrophanthidin*, $C_{25}H_{34}O_4$, forms needles which sinter above 210°, m. p. 216—218°, $[\alpha]_D^{23}$ $-101{\cdot}3°$ in chloroform. *Dianhydrodihydrostrophanthidin* forms needles sintering at 190°, m. p. 193—199°, $[\alpha]_D^{4}$ $-184°$ in chloroform. The *oxime* forms prisms, m. p. 291—292°. C. R. H.

Tannins and Similar Substances. XVI. Stereoisomeric Catechins. IV. K. FREUDENBERG and L. PURRMANN (*Annalen*, 1924, **437**, 274—285; cf. A., 1923, i, 697).—The previously studied relations of the stereoisomeric catechins and epicatechin have been further investigated with larger quantities of material, a good yield of *l*-epicatechin, together with a little *dl*-catechin, being obtained from the heartwood of *Acacia catechu*. The transformation of *d*-catechin and of *l*-epicatechin to *l*-catechin and *dl*-catechin is promoted considerably by the presence of a trace of potassium hydrogen carbonate. The epicatechins are rather less stable than the corresponding catechins, and *dl*-epicatechin is only obtained pure by mixing the *d*- and *l*-forms. The active forms are easily separated from the racemates and are recognised by their rotatory powers in alcohol, in the case of the epicatechins, and in aqueous acetone, disappearing in alcohol, in the case of the catechins. The data now available lead to the conclusion that the acacatechin examined by Perkin (T., 1905, **87**, 398) consisted largely of *dl*-catechin admixed with some *l*-epicatechin, a conclusion which has been confirmed by a series of mixed melting points of Perkin's derivatives with those of *dl*-catechin, and by the observation that *dl*-catechin always sinters 60—70° below its m. p. (205—210°) when epicatechin is present. The "catechin C" of Perkin and Yoshitake (T., 1902, **81**, 1167) obtained from Gambier catechin, m. p. 235—237° [disazobenzene derivative, m. p. 215—217° (decomp.)] appears to be identical with *d*-epicatechin, m. p. 245° (decomp.) [disazobenzene derivative, m. p. 216—218° (decomp.)], and the authors have isolated a small quantity of *d*-epicatechin from Gambier catechin. Bromotetramethyl-*d*-catechin has m. p. 172—173°, without decomposition (cf. Kostanecki and Krembs, A., 1902, i, 637), and the acetate, m. p. 174—175°. dl-*Catechin tetramethyl ether* melts at 142°, the *monoacetate* at 134—135°, and the *toluenesulphonate* at 156—157°. dl-*Catechin pentabenzoate* melts at 181—182°, and the *pentamethyl ether* at 110—111°. d-*Epicatechin tetramethyl ether* melts at 93—94° and the *acetate* at 91—92°. The melting points and rotatory powers of the stereoisomeric catechins and epicatechins and their derivatives are tabulated.

R. B.

Anilino-flavones. K. von Auwers and O. Jordan (*J. pr. Chem.*, 1924, [ii], **107**, 330—357).—Auwers and Müller (A., 1909, i, 222) obtained by heating together in toluene solution aniline and 3-chloroacetyl-*p*-tolyl benzoate, *N*-benzoyl-3-phenylglycyl-*p*-cresol, and a by-product, m. p. 133—134°, now identified as 3-*anilino*-6-*methylflavone* (annexed formula). When the solvent used is benzene scarcely any of this product is formed, whilst if it be xylene, 22% of the theoretical yield is obtained. The authors discuss the mechanism of the reaction, and describe experiments on the stability of compounds of the type R·CO·CH_2·NH·Ph, the results of which bear on the question. 3-Anilino-6-methylflavone yields an unstable *hydrochloride* and *acetyl* (m. p. 165—167°) and *benzoyl* (m. p. 154—155°) derivatives, but no alkyl derivatives; neither can the latter be obtained by condensing 3-chloroacetyl-*p*-tolyl benzoate with, *e.g.*, methylaniline. With bromine in carbon disulphide it gives an unstable *compound*, m. p. 80—85°, and when the reaction mixture is heated, the p-*bromoanilinoflavone*, m. p. 154°, is formed, identical with the product of interaction of *p*-bromoaniline and 3-chloroacetyl-*p*-tolyl benzoate. When the flavone is heated with alcoholic sodium ethoxide, it breaks up, giving aniline, benzoic acid, *p*-hydroxytoluic acid, and benzanilide, together with unidentified products, whilst with the cold reagent partial conversion to *N*-benzoyl-3-phenylglycyl-*p*-cresol takes place.



Analogous flavone derivatives were prepared. The yields were poor, being mostly about 20% of the theoretical. *o*-Chloroacetyl-*m*-methoxyphenyl benzoate failed to react satisfactorily. 3-Chloroacetyl-*p*-tolyl benzoate and *o*-toluidine gives 3-*toluidino*-6-*methylflavone*, yellow needles, m. p. 107—108°; the corresponding compound with m-*toluidine* has m. p. 118—119°; with p-*toluidine*, m. p. 149·5°. 3-Chloroacetyl-*p*-tolyl *p*-methoxybenzoate yields with aniline 3-*anilino*-4′-*methoxy*-6-*methylflavone*, yellow needles, m. p. 151—152°, and the p-*anisidino*-analogue has m. p. 165—166°.

o-Chloroacetyl-*p*-methoxyphenyl benzoate forms colourless needles, m. p. 96—97°, and reacts with aniline to yield normally a *flavone*, m. p. 133—134°, and analogous products with o-*toluidine* (yield exceptional, viz., 45%, m. p. 162·5—163°), with m-*xylidine* (m. p. 95—96·5°), and with p-*anisidine* (m. p. 120—121°). o-*Chloroacetyl*-p-*methoxyphenyl anisate*, colourless needles, has m. p. 109·5—110·5°, but yields scarcely any flavone. 3-*Anilinoflavone*, the simplest representative of the group, was obtained from o-*chloroacetophenyl benzoate* (colourless rods, m. p. 81—82°) and aniline. It forms yellow needles, m. p. 116°.

The following compounds are also described : m-*acetyl*-p-*ethoxytoluene*, m. p. 44—45°; *ethyl* o-*ethoxytoluate*, b. p. 143—143·5°/10 mm.; N-*methyl*-3-*phenylglycyl*-p-*cresol*, m. p. 87—88°; and its *benzoyl* derivative, m. p. 120—121°; 3-α-*bromopropionyl*-p-*tolyl anisate*, m. p. 86·5—87·5°; 3-α-*methylphenylglycyl*-p-*cresol*, m. p. 96·5—97·5°; 2-*chloroacetyl*-5-*methoxyphenyl anisate*, m. p. 152·5—153°; N-*acetyl*-3-*phenylglycyl*-p-*tolyl acetate*, m. p. 123—124°; and N-*acetyl*-3-*phenylglycyl*-p-*cresol*, m. p. 152—153°. W. A. S.

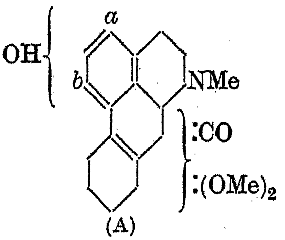
Preparation of Synthetic *d*- and *l*-ψ-Cocaine. E. MERCK (Brit. Pat. 210050).—Racemic ψ-ecgonine methyl ester (cf. Willstätter and others, A., 1921, i, 122, and this vol., i, 70) is resolved and the optically active esters obtained are benzoylated with benzoic anhydride. Specimen resolutions by means of *d*-α-bromocamphor-β-sulphonic acid, *d*-α-bromocamphor-π-sulphonic acid, and malic acid are described. *d*-ψ-Ecgonine methyl ester *d*-α-bromocamphor-β-sulphonate forms crystals resembling a coffin-lid in shape and having m. p. 198° and $[\alpha]_D^{20}$ +71·5° (in 5% aqueous solution); it yields *d*-ψ-ecgonine methyl ester melting at 115° and identical with the natural product. Benzoylation of this ester with benzoic anhydride in benzene solution yields *d*-ψ-cocaine, m. p. 45°. The hydrochloride of the latter is sparingly soluble in water and has m. p. 205° and $[\alpha]_D^{20}$ +43° (in 5% solution). *l*-ψ-Ecgonine methyl ester *d*-α-bromocamphor-π-sulphonate has m. p. 243° and $[\alpha]_D^{20}$ +43·7° (in 5% aqueous solution). *l*-ψ-Ecgonine methyl ester has $[\alpha]_D^{20}$ −14·8° (in 10% methyl-alcoholic solution; it yields *l*-ψ-cocaine on benzoylation and the *r*-ester, m. p. 128°, when mixed with *d*-ψ-ecgonine methyl ester. *d*-ψ-Ecgonine methyl ester *d*-α-bromocamphor-π-sulphonate is a readily soluble salt, m. p. 130°. *l*-ψ-Ecgonine methyl ester *l*-malate is sparingly soluble and has m. p. 176° and $[\alpha]_D^{20}$ −18·2° (in 5% aqueous solution). The corresponding *d*-ester *l*-malate is soluble and melts at 142°.

W. T. K. B.

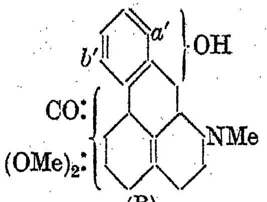
Preparation of Tropacocaine from Javanese Coca Leaves. K. HARA and T. SAKAMOTO (*J. Pharm. Soc. Japan*, 1924, **503**, 33—38).—Tropacocaine is soluble in dilute ammonia; its hydrobromide is insoluble in water. Utilising this property, the authors have prepared tropacocaine hydrochloride from petroleum extracts of coca leaves produced in Java (yield about 1% of the crude extract). The residue, from which tropacocaine has thus been prepared, is then used as material for preparing cocaine. [Cf. *B.*, 1924, 653.] K. K.

Alkaloids of *Datura alba*, Nees. S. OSADA (*J. Pharm. Soc. Japan*, 1924, No. 504, 89—93).—The seeds of *Datura alba*, Nees, from the wild Formosa plant, on extraction with warm 96% alcohol, gave about 12% of brown oil, in which the following alkaloids were identified : *l*-scopolamine 0·24%, hyoscyamine 0·02%, and atropine (as gold double salt) 0·0026%. A small amount of a *base* which gives a *chloroaurate*, m. p. 220°, was also obtained. K. K.

Alkaloids of Sinomenium and Cocculus. II. Constitution of Sinomenine. E. Ochiai (*J. Pharm. Soc. Japan*, 1924, No. 503, 8—23; cf. Kondo, Ochiai, and Nakajima, A., 1923, i, 1222; K. Goto, *J. Chem. Soc. Japan*, 1923, **44**, 795).—When treated in glacial acetic acid solution with bromine, sinomenine hydrochloride gives two *monobromides*; one, white needles, melts at 205° (decomp.), and the other, needles (obtained in larger amount), at 138° (decomp.). Both give a green coloration with ferric chloride. The iodine values (Wijs) of sinomenine and of its benzoyl derivative were found to be 143·9 and 53·89, respectively, whence sinomenine probably has the formula $C_{19}H_{23}O_4N$, and contains one ethylenic linking. When reduced by Skita's method, sinomenine affords *dihydrosinomenine*, $C_{19}H_{25}O_4N$, m. p. 199° (decomp.), $[\alpha]^{16}_{D}$ $+170·5°$. Sinomenine gives an *oxime*, m. p. 254°, and a *semicarbazone*, m. p. 264°, both of which give a green coloration with ferric chloride. Methyl- and dihydrosinomenine also give *semicarbazones*, the former of m. p. 252°, the latter of m. p. 207°. Thus, one oxygen atom in sinomenine is present in a carbonyl radical, the others in two methoxyl radicals and one phenolic hydroxyl radical. When sinomenine is heated with excess of benzoic anhydride in a sealed tube at 150—160° for 6 hours, a colourless, optically inactive *substance*, $C_{25}H_{22}O_5$ (m. p. 206°), is produced, which is insoluble in acids and alkalis and contains one ethylenic linking, probably produced by the breaking of a nucleus. When treated with ethyl chloroformate in alkaline solution, sinomenine gives a light non-crystallisable *substance*, $C_{25}H_{32}O_8NCl$, decomp. at 183°, $[\alpha]^{17}_{D}$ $-108·4°$. When distilled with excess of zinc dust, sinomenine affords considerable quantities of phenanthrene, and also of trimethylamine, and a small amount of an oily *substance* having an odour of quinoline. From these facts the author proposes one of the two following formulæ for sinomenine:



(A)



(B)

K. K

Formation of Quaternary Ammonium Salts. II. E. de B. Barnett, J. W. Cook, and W. C. Peck (*J. Chem. Soc.*, 1924, **125**, 1035—1040).—The formation of quinolpyridinium salts, which had previously been shown to occur when *p*-benzoquinone was heated with the pyridine salts of inorganic acids, has now been extended to salts of organic acids. Reaction takes place with difficulty, and the products can only be purified viâ the picrates.. *Dihydroxyphenylpyridinium phenylacetate*, brown leaflets, m. p. 160°, was obtained by interaction of *p*-benzoquinone, pyridine, and phenylacetic acid.

The interaction of ethylenic compounds and pyridine–bromine mixtures has also been investigated. Well-defined *vic.*-bromopyridinium salts were obtained from anethole, *iso*safrole, *cyclo*hexane, and stilbene, the respective compounds formed being: β(or α)-*bromodihydroanethole*-α(or β)-*pyridinium bromide*, m. p. 170—172° (decomp.); β(or α)-*bromodihydrosafrole*-α(or β)-*pyridinium bromide*, m. p. 193° (decomp.); 1-*bromo*cyclo*hexane*-2-*pyridinium bromide*, m. p. 165—170°; β-*bromo*-αβ-*diphenylethylpyridinium bromide*, m. p. 190—193°, which after boiling with water and precipitated calcium carbonate gave β-*dihydroxy*-αβ-*diphenylethylpyridinium bromide*, m. p. 238—240°. Cinnamic acid yielded α-*bromo*-β-*phenylpropionic acid*-β-*pyridinium bromide*, m. p. 193—198° (decomp.), which on boiling with water or alcohol was converted into a *betaine*, m. p. 178—180°. *Methyl* α-*bromo*-β-*phenylpropionate*-β-*pyridinium bromide*, m. p. 178° (decomp.), and the corresponding *ethyl* ester, m. p. 157—158° (decomp.), were obtained from methyl and ethyl cinnamate respectively. Both of these esters when treated with ammonia gave methyl and ethyl α-bromocinnamates in 80—90% yield. The product obtained from safrole was too soluble to be isolated and probably consists of a dipyridinium salt.

C. J. S.

Synthesis of Pyridine-ketones from Hydroxymethylene-acetone and -acetophenone. E. Benary and H. Psille (*Ber.*, 1924, **57**, [B], 828—834).—An ethereal solution of ω-formylacetophenone was added to a saturated solution of ammonium acetate in glacial acetic acid and allowed to stand. Di-β-benzoylvinylamine, $(CHBz{:}CH)_2NH$, separated (Claisen's "ammonia compound of benzoylacetaldehyde," A., 1888, 690) which gave 1 : 3-diphenylpyrazole with phenylhydrazine (cf. Knorr, A., 1893, i, 230). From the acetic acid mother-liquor a base, $C_{18}H_{13}ON$, was recovered, colourless crystals, m. p. 89·5°; its *oxime* (m. p. 183—184°) with phosphorus pentachloride gave an *anilide*, $C_{18}H_{14}ON_2$, leaflets, m. p. 199°, which hydrolysed to an acid, $C_{12}H_9O_2N$, colourless needles, m. p. 220—229°, yielding 2-phenylpyridine (picrate, m. p. 175°) on heating with lime. The acid was therefore 2-*phenylpyridine*-5-*carboxylic acid*, and the original base 3-*benzoyl*-6-*phenylpyridine*. The latter is slowly attacked by permanganate and is unaffected by fused potassium hydroxide; it forms a yellow *picrate*, m. p. 175°; a colourless *hydrochloride*, m. p. 202°; a *nitrate*, m. p. 135—136°, and a *sulphate*, m. p. 137—138°. 3-Benzoyl-6-phenylpyridine with alcohol and zinc dust afforded 2-*phenyl*-5-α-*hydroxybenzylpyridine*, $OH{\cdot}CHPh{\cdot}C_5H_3NPh$, rhombohedra, m. p. 115—116° (*picrate*, m. p. 175—176°; *hydrochloride*, m. p. 173—174°). With phosphorus pentachloride the carbinol yielded 2-*phenyl*-5-α-*chlorobenzylpyridine*, m. p. 79°, reduced by acetic acid and zinc dust to *2-phenyl-5-benzylpyridine*, as leaflets, m. p. 63—63·5° (*picrate*, m. p. 145—146°; *hydrochloride*, m. p. 170°).

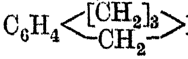
Treatment of sodium formyl-acetone with ammonium acetate and glacial acetic acid gave 3-acetyl-6-methylpyridine, b. p. 231—232° (cf. Knudson, A., 1895, i, 564), oxime, m. p. 182°. *Hydrochloride*, hygroscopic; *picrate*, m. p. 190°; *chloromercurate*, $C_8H_9ON{\cdot}HgCl_2$, m. p. 128°, and *methiodide*, m. p. 156·5°. On warming with nitric acid (1·42) 5-acetyl-2-methyl pyridine yielded *2-methylpyridine-5-carboxylic acid nitrate*, m. p. 170—171°, which on distillation with lime yielded pyridine but no α-picoline; the nitrate yielded a dark green *copper* salt, $(C_5H_3NMe{\cdot}CO_2)_2Cu,(AcO)_2Cu$, from which the free acid was obtained, m. p. 207° (cf. Ladenberg, *Ann.*, 1888, **247**, 43). 3-Acetyl-6-methylpyridine, when condensed with formic ester by means of sodium ethoxide, gave the orange *sodium* salt of *5-hydroxyacryl-2-methylpyridine*, $C_5H_3NMe{\cdot}CO{\cdot}CH{:}CH{\cdot}OH$ (*copper* salt, light olive-green). *5-Hydroxyacryl-2-methylpyridine* was obtained as an unstable yellow oil by the action of sulphuric acid on the copper salt; it gave no precipitate with picric acid or with mercuric chloride. The sodium salt reacted with aniline to form *5-hydroxyacryl-2-methylpyridine-anil*, $C_5H_3NMe{\cdot}CO{\cdot}CH{:}CH{\cdot}NHPh$, as pale yellow needles, m. p. 154—155°.

F. A. M.

New Method in the *iso*Quinoline and its Ring Homologous Series. J. VON BRAUN, G. BLESSING, and R. S. CAHN (*Ber.*, 1924, **57**, [*B*], 908—912).—Ring closure with the formation of tetrahydro*iso*quinolines and *as*-homotetrahydro*iso*quinolines is readily effected by the successive action of phosphorus pentachloride and aluminium chloride on acylated derivatives of β-phenylethyl- and γ-phenylpropyl-glycine.

The *benzenesulphonyl* derivative of β-phenylethylglycine, $CH_2Ph{\cdot}CH_2{\cdot}N(SO_2Ph){\cdot}CH_2{\cdot}CO_2H$, m. p. 122°, is dissolved in nitrobenzene and treated successively with phosphorus pentachloride and aluminium chloride, thus giving *2-benzenesulphonyltetrahydro*isoquinoline, m. p. 154° (yield 80%), from which tetrahydro*iso*quinoline is readily obtained, the over-all yield being about 50% of that theoretically possible. β-*m*-Tolylethylamine is converted by ethyl bromoacetate in ethereal solution into *ethyl* β-m-*tolylethylaminoacetate*, b. p. 165—167°/11 mm., which is transformed by concentrated hydrochloric acid into β-m-*tolylethylglycine hydrochloride*, m. p. 212—214°. The latter compound is converted into β-m-*tolylethylbenzenesulphonylglycine*, m. p. 105—106°, from which *2-benzenesulphonyl-6-methyltetrahydro*isoquinoline, m. p. 102°, is derived. 6-*Methyltetrahydro*isoquinoline has b. p. 110°/11 mm., 255—256°/758 mm., d_4^8 1·0235; the *hydrochloride*, m. p. 195—197°, *picrate*, m. p. 205°, *nitroso* derivative, m. p. 98°, and quaternary *methiodide*, m. p. 144—145°, are described.

Ethyl γ-phenylpropylaminoacetate, b. p. 167—170°/11 mm., is transformed into *γ-phenylpropylglycine hydrochloride*, decomp. 201°. The non-crystalline *benzenesulphonyl* derivative of γ-phenylpropylglycine and the corresponding *toluene*-p-*sulphonyl* compound, m. p.

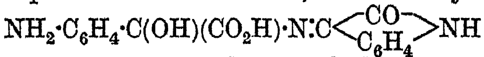
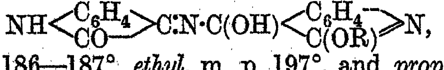
98—100°, are described. The latter substance is readily transformed in the usual manner into *toluene*-p-*sulphonyl*-as-*homotetrahydro*iso*quinoline*, m. p. 135°, from which the free base,  $C_6H_4<\genfrac{}{}{0pt}{}{[CH_2]_3}{CH_2}>NH$, is obtained by hydrolysis. H. W.

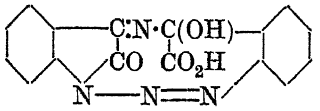
Preparation of Compounds Related to the Acridines. British Dyestuffs Corporation, W. H. Perkin, and G. R. Clemo (Brit. Pat. 214756).—Dihydroacridines are obtained by reducing the corresponding acridones with sodium amalgam in hot alcoholic solution in presence of sodium hydrogen carbonate, carbon dioxide being passed through the reacting mixture. After removal of the alcohol, the dihydroacridine is precipitated by adding water. The dihydroacridines yield the corresponding acridines when oxidised (*e.g.*, with nitrous acid or chromic acid).

9-Aminodihydroacridine (almost colourless hairs, m. p. 114°), obtained by reducing 9-nitroacridone with sodium amalgam, is converted into 9-aminoacridine by acylating (to protect the amino group), oxidising as above, and hydrolysing the product.

W. T. K. B.

Products of the Action of Ammonia on Isatin. A. Reissert and H. Hoppmann (*Ber.*, 1924, 57, [*B*], 972—981).—The constitution of many of the compounds isolated by Laurent in the years 1842 and 1845 has been elucidated.

Isatin ammonia [*3-amino-3-hydroxy-2-ketodihydroindole*], the primary product of the action of isatin and ammonia, is obtained when ammonia is passed into an ice-cold, alcoholic suspension of isatin until further separation of crystals does not occur; it readily loses ammonia when exposed to the air. If the stream of ammonia is interrupted as soon as the isatin is completely dissolved and the solution is then preserved, isatin-3-imide (Laurent's imesatin) is obtained in dark yellow, rectangular prisms, m. p. 175—176°, which is considerably more stable than the corresponding 2-compound. If the action of alcoholic ammonia on isatin is very protracted or if concentrated aqueous ammonia is used, 3-isatinimidyl-*o*-aminomandelic acid,  $NH_2{\cdot}C_6H_4{\cdot}C(OH)(CO_2H){\cdot}N{:}C<\genfrac{}{}{0pt}{}{CO}{C_6H_4}>NH$ (Laurent's imasatic or isamic acid), is produced, which is more conveniently prepared by boiling isatin with ammonium acetate solution. It forms red, prismatic crystals, m. p. 164—165° (decomp.). The *ammonium* and *aniline* salt, m. p. 198°, and the o-*benzoyl* derivative, m. p. 188°, are described. The constitution of the acid is established by its synthesis from isatin-3-imine and ammonium isatate. The acid could not be converted into its cyclic anhydride, but when esterified, yields derivatives thereof of the type  $NH<\genfrac{}{}{0pt}{}{C_6H_4}{CO}>C{:}N{\cdot}C(OH)<\genfrac{}{}{0pt}{}{C_6H_4-}{C(OR)}\gg N$, of which the *methyl*, m. p. 186—187°, *ethyl*, m. p. 197°, and *propyl*, m. p. 181°, compounds are described; they are reconverted by sodium hydr-



oxide into the acid. Diazotisation of the latter substance in aqueous solution leads to the production of 3-*isatinimidyl*-o-N-*azomandelic acid* (annexed formula), m. p. about 140° (decomp.). If, however, ethyl nitrate is used, both hydroxy groups are esterified with formation of *ethyl* 3-*isatinimidyl*-o-N-*azophenylethoxyacetate*, m. p. 214—215°, which is hydrolysed to the corresponding *acid*, m. p. 195°. *Ethyl* 3-*isatinimido*-o-N-*azomandelate* has m. p. 214—215°.

When isatin is subjected to the prolonged action of aqueous ammonia, a phenolic substance (Laurent's imasatin), m. p. 230° after softening at 200°, is produced in addition to 3-isatinimidyl-*o*-aminomandelic acid. Since it can be synthesised by warming isatin and isatinimine in alcoholic solution, it is regarded as 3-isatinimidyl-3-dioxindole, although its genetic relationship to 3-isatinimidyl-*o*-aminomandelic acid could not be established. The *monobenzoyl* derivative decomposes above 240°.

Laurent's amasatin or isamide can be prepared by heating ammonium 3-isatinamidyl-*o*-aminomandelate, and is therefore 3-isatinimidyl-*o*-aminomandelamide; the corresponding *anilide* has m. p. 168°.

When isatin is treated with ammonia under pressure at the atmospheric temperature, Sommaruga's "di-iminoisatin or isatindiamine" is produced, which appears to be a polymeric isatinimine. At 100°, "hydroxydiaminodi-iminoisatin," $C_{16}H_{14}O_3N_6$, is also formed. H. W.

Preparation of a Monochloro Derivative of Antipyrine. A. LEULIER (*J. Pharm. Chim.*, 1924, [vii], **29**, 447—449).—A *monochloroantipyrine*, $C_{11}H_{11}ON_2Cl$, faintly yellow needles, m. p. 123—124°, is obtained by dissolving antipyrine in a 20% solution of chlorine and keeping the mixture for ¼ hour. The yield is smaller if sodium hypochlorite is used. Its aqueous solution gives a red coloration with ferric chloride. W. T. K. B.

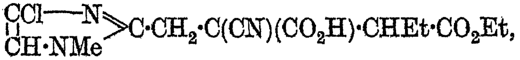
Synthesis of Pyrazolealdehydes. II. C. A. ROJAHN and A. SEITZ (*Annalen*, 1924, **437**, 297—308; cf. this vol., i, 91).—The methods previously found successful in the preparation of pyrazole-4-aldehydes have been used in the synthesis of the 3(5)-aldehydes. The reduction of the acid chlorides affords, besides the aldehyde, oily by-products, which were found to be pyrazoles containing a methyl group less than was expected, carbon monoxide being lost in the reaction. It remains uncertain whether the decomposition is $R{\cdot}COCl \longrightarrow RH+CO+HCl$ or $R{\cdot}COH \longrightarrow RH+CO$. The 3- and 5-pyrazolealdehydes are for the most part oils with the general reactions of aromatic aldehydes. They do not undergo the benzoin or Cannizzaro reaction, the latter only affording traces of the carboxylic acid and resinous products (cf. Fischer and Zerweck, A., 1923, i, 364). 1-Phenyl-5-methylpyrazole-3-carboxylic acid with thionyl chloride yields 1-*phenyl*-5-*methyl*-

pyrazole-3-*carboxyl chloride*, m. p. 85° (*anilide*, m. p. 138°), which on reduction in xylene with palladium–barium sulphate catalyst, either with or without "sulphured" quinoline, gives 60—70% of the theoretical yield of 1-*phenyl*-5-*methylpyrazole*-3-*aldehyde*, d^{15}= 1·155 (*phenylhydrazone*, m. p. 173°; *semicarbazone*, m. p. 183°; *oxime*, m. p. 166°; *aminoguanidine nitrate derivative* ($+1H_2O$), $C_{12}H_{17}O_4N_7$, m. p. 155°). On shaking the bisulphite compound with aqueous potassium cyanide, the *hydroxynitrile* is formed, yellow needles, m. p. 121°. 1-Phenylpyrazole-5-carboxylic acid similarly yields 1-*phenylpyrazole*-5-*carboxyl chloride*, long needles, m. p. 53°, which on reduction with the catalyst and in the presence of a glowing copper spiral yields 1-*phenylpyrazole*-5-*aldehyde* (*semicarbazone*, m. p. 168°; *oxime*, m. p. 177°, *aminoguanidine nitrate derivative*, $C_{11}H_{12}N_6,HNO_3$, m. p. 192°), and a little 1-phenylpyrazole. By the condensation of ethyl acetylpyruvate with phenylhydrazine (cf. Claisen, A., 1894, i, 346) besides the 1-phenyl-5-methylpyrazole-3-carboxylic acid a higher melting product was obtained which with thionyl chloride yields 1-*phenyl*-3-*methylpyrazole*-5-*carboxyl chloride*, m. p. 39—41°, identified by conversion to the corresponding acid and amide. On reduction in the presence of a glowing copper spiral, 1-phenyl-3-methylpyrazole was obtained together with 1-*phenyl*-3-*methylpyrazole*-5-*aldehyde* (*aminoguanidine nitrate* derivative, m. p. 196°), which yields two *semicarbazones*, m. p. 166° and 195°, and two *oximes*, m. p. 146° and 179°, partial transformation of the lower-melting isomeride taking place in each case on seeding. 1-Phenyl-5-methylpyrazole-3-carboxylic acid on bromination in acetic acid solution yields 4-*bromo*-1-*phenyl*-5-*methylpyrazole*-3-*carboxylic acid*, white needles, m. p. 184°, converted to 4-*bromo*-1-*phenyl*-5-*methylpyrazole*-3-*carboxyl chloride*, long, lustrous needles, m. p. 78°, by thionyl chloride; the chloride on reduction yields 4-*bromo*-1-*phenyl*-5-*methylpyrazole*, b. p. 130° (*methiodide*, m. p. 206°), which was also obtained by brominating 1-phenyl-5-methylpyrazole, and 4-*bromo*-1-*phenyl*-5-*methylpyrazolealdehyde*, m. p. 71° (*oxime*, m. p. 194°; *semicarbazone*, m. p. 217°; *aminoguanidine nitrate* derivative, $+1H_2O$, m. p. 193°), the bisulphite liquor used in the separation yielding also some 4-*bromo*-1-*phenyl*-5-*methyl*-3-*hydroxymethylpyrazole*, m. p. 166—167° (*acetate*, m. p. 108°). 4-*Chloro*-1-*phenyl*-5-*methylpyrazole*-3-*carboxylic acid*, m. p. 221°, was obtained by the action of chlorine on a cold chloroform solution of 1-phenyl-5-methylpyrazole-3-carboxylic acid. R. B.

Conversion of Diketopiperazines into the corresponding Piperazines. E. Abderhalden, E. Klarmann, and E. Schwab (*Z. physiol. Chem.*, 1924, **135**, 180—187).—Piperazine hydrochloride was prepared from glycine anhydride by reduction with sodium, amyl alcohol, etc. *iso*Butylpiperazine dihydrochloride was similarly prepared from leucylglycine anhydride using sodium and ethyl alcohol. *Dibenzoylisobutylpiperazine* does not melt at 300°. The yields throughout were not good. The authors discuss the possibilities of the addition of amino-acids occurring through the imino group or through the hydroxyl group of the tautomeric form of diketopiperazines. E. M. C.

Preparation of Compounds of Diketopiperazines with Amino-acids or Polypeptides. II. E. ABDERHALDEN and E. KLARMANN (*Z. physiol. Chem.*, 1924, **135**, 199—202).—Neither alanylglycine anhydride nor leucylglycine anhydride reacts with chloroacetyl chloride (cf. A., 1923, i, 1025). Glycine anhydride and α-bromo-γ-methylvaleryl chloride gave 1 : 4-*di*(α-*bromo*-γ-*methylvaleryl*)-2 : 5-*diketopiperazine*, m. p. 145°, which with ammonia gave glycine anhydride and leucinamide. E. M. C.

Synthetic Experiments in the Glyoxaline Group. A. SONN, E. HOTES, and H. SIEG (*Ber.*, 1924, **57**, [*B*], 953—959).—4-Chloro-1-methylglyoxaline is converted by formaldehyde at 130—140° into 4-chloro-1-methyl-2-hydroxymethylglyoxaline, m. p. 120° (cf. Sarasin, A., 1923, i, 711); the picrate, m. p. 150—151°, *hydrochloride*, m. p. 162°, additive *compound* with mercuric chloride, m. p. 161—162°, the *benzoate*, m. p. 75°, and its *picrate*, m. p. 167°, are described. The base is transformed by thionyl chloride into 4-*chloro*-1-*methyl*-2-*chloromethylglyoxaline hydrochloride*, m. p. 167—168° (corresponding *picrate*, m. p. 156—157°), which is reduced by zinc dust and glacial acetic acid to 4-*chloro*-1 : 2-*dimethylglyoxaline*, a yellow liquid (*picrate*, m. p. 175—176°), and by phosphorus and hydriodic acid to 1 : 2-dimethylglyoxaline. The catalytic reduction of 4-chloro-1-methyl-2-hydroxymethylglyoxaline yields 1-methyl-2-hydroxymethylglyoxaline, which is identified as the *picrate*, m. p. 136—137°. The following compounds are obtained from 4-chloro-1-methyl-2-chloromethylglyoxaline: 4-*chloro*-1-*methyl*-2-*ethoxymethylglyoxaline*, a pale yellow, mobile liquid, and its *picrate*, m. p. 101—102°; 4-*chloro*-1-*methyl*-2-*methylaminomethylglyoxaline picrate*, m. p. 178°; 4-*chloro*-1-*methyl*-2-*dimethylaminomethylglyoxaline hydrochloride*, m. p. 198° (decomp.); 4-*chloro*-1-*methyl*-2-*anilinomethylglyoxaline*, m. p. 125—126°, and its *picrate*, m. p. 170—171°; 4-*chloro*-2-p-*ethoxyanilino*-1-*methylglyoxaline*, m. p. 114—115°. 4-*Chloro*-1-*methyl*-2-*cyanomethylglyoxaline*, m. p. 128° after softening at 110° (*picrate*, m. p. 177—178°) is reduced by sodium and alcohol to 4-*chloro*-1-*methyl*-2-*aminoethylglyoxaline*, which is analysed as the *picrate*, m. p. 176° after previous softening. The action of 4-chloro-1-methyl-2-chloromethylglyoxaline on the sodium derivative of ethyl α-cyano-β-ethylsuccinate and subsequent hydrolysis of the product with boiling concentrated hydrochloric acid leads to the isolation of 4-*chloro*-1-*methyl*-2-β-*cyano*-γ-*carboxy*-n-*amylglyoxaline hydrochloride*, plates, decomp. 250° after darkening at 242° and (?) (γ)ethyl hydrogen β-cyano-α-4-chloro-1-methyl-2-glyoxalinylpentane-βγ-dicarboxylate,



$$\left.\begin{matrix}\text{CCl}—\text{N}\\ \text{CH}\cdot\text{NMe}\end{matrix}\right>\text{C}\cdot\text{CH}_2\cdot\text{C(CN)(CO}_2\text{H)}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et},$$

m. p. 128° (*picrate*, m. p. 163—164° after slight previous softening). 4-Chloro-1-methyl-2-chloromethylglyoxaline gives a non-crystalline condensation product with ethyl sodiomalonate which is transformed by successive bromination, hydrolysis, and elimination of carbon dioxide into a non-homogeneous, brominated monocarboxylic acid; the latter is converted by saturated aqueous ammonia at 50—60° into *ammonium α-amino-β-4-chloro-5-bromo-1-methylglyoxalinylpropionate*, m. p. 205—206° after previous softening (*picrate* of amino-acid, m. p. 231°).

Dimethyloxamide is converted by phosphorus pentabromide into *dibromo-1-methylglyoxaline*, colourless needles, m. p. 78—79° (picrate, m. p. 146°). H. W.

Stable and Labile Acyl Derivatives of the Indazoles. K. von Auwers and H. G. Allardt (*Annalen*, 1924, **438**, 1—33).—The 2-acyl derivatives of indazole and substituted indazoles have been examined, especially with regard to the stabilities of the labile forms (cf. A., 1919, i, 455; 1920, i, 638, 640; 1921, i, 806). The general method of the preparation of the labile forms is by the action of the silver salt of the indazole on the corresponding indazole in dry ether at 0° or by the interaction of the indazole and the acid chloride in dry pyridine or ether at 0°. The stable form is produced by the interaction of the sodium salt and the acid chloride under similar conditions. Many acyl indazoles are rather easily hydrolysed, especially the labile form; with hydrogen chloride in dry ether, the latter give indazole hydrochloride, whereas the stable form is unchanged after some hours. The effect of the acyl group on the stability of the labile acylindazoles has been examined. Preliminary experiments were carried out in sealed tubes, and the relative stabilities of some of the compounds are given as follows: *o*-nitrobenzoyl-, *o*-nitrocinnamoyl-, 2-nitro-5-bromobenzoyl- (stable after 1 year); *p*-nitrobenzoyl-, phenylacetyl-, carbonyl-; succinyl- (partly converted), *iso*butyryl- (converted in a few days), crotonyl- (1 day), *n*-butyryl- (somewhat more stable), propionyl- and acetyl- (unstable).

The following stable and labile 2-acyl derivatives have been examined, and the following values, amongst others, are given (*s*=stable; *l*=labile; rotatory dispersions are also given when refractive indices are given).

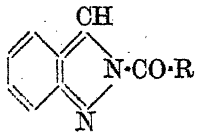
(*s*)-2-Acetylindazole, $d_4^{16\cdot8}$ 1·1886, $n_{\mathrm{He}}^{16\cdot8}$ 1·58955; (*l*)-2-acetyl indazole, $d_4^{18\cdot7}$ 1·1007, $n_{\mathrm{He}}^{18\cdot7}$ 1·62682; (*s*)-2-*chloroacetylindazole*, monoclinic prisms, m. p. 82—83°, b. p. 162°/10 mm., $d_4^{99\cdot6}$ 1·2636, $n_{\mathrm{He}}^{99\cdot6}$ 1·57393; (*s*)-2-*dichloroacetylindazole*, stout white needles, m. p. 80—82°, b. p. 168—170°/13 mm.; (*s*)-2-*trichloroacetylindazole*, small prisms, m. p. 116—117°, hydrolysed by ethyl alcohol; (*s*)-2-*cyanoacetylindazole*, colourless crystals, m. p. 164—165°; (*s*)-2-*bromoacetylindazole*, fine needles, m. p. 73—74°; (*s*)-2-*α-bromopropionylindazole*, needles, m. p. 65—66°; (*s*)-2-n-*butyrylindazole*, colourless prisms, m. p. 61°, b. p. 150°/15 mm., $d_4^{33\cdot5}$ 1·1090, $n_{\mathrm{He}}^{33\cdot5}$ 1·55854; (*l*)-2-n-*butyrylindazole*, small, glassy prisms, m. p. 86—87°, easily converted to stable form, $n_{\mathrm{He}}^{12\cdot85}$ 1·62593 (in quinoline); (*s*)-2-iso*butyrylindazole*, oil, b. p. 132°/11 mm., $d_4^{12\cdot8}$ 1·1136, $n_{\mathrm{He}}^{12\cdot8}$ 1·56534; (*l*)-2-iso*butyrylindazole*, oil, easily converted to α-form by ethereal hydrogen chloride, $d_4^{13\cdot0}$ 1·1159, $n_{\mathrm{He}}^{13\cdot0}$ 1·57671; (*s*)-2-iso*valerylindazole*, b. p. 148—150°/11 mm., $d_4^{16\cdot3}$ 1·0879, $n_{\mathrm{He}}^{16\cdot3}$

1·55466; (*l*)-2-iso*valerylindazole*, needles, m. p. 64° (approx.), unstable; (*s*)-2-*crotonylindazole* can only be prepared from the labile isomeride by standing over sulphuric acid, m. p. 78—80°; (*l*)-2-*crotonylindazole*, white, very hygroscopic crystals, m. p. 102°, resinifying on warming at 100°; (*s*)-2-Δ^{γ}-*pentenoylindazole*, b. p. 168—170°/16 mm., $d_4^{22\cdot6}$ 1·1172, $n_{\mathrm{He}}^{22\cdot6}$ 1·57070; (*s*)-2-*nitrobenzoylindazole*, fine needles, m. p. 186—187°; (*l*)-2-*nitrobenzoylindazole*, fine, yellowish-green needles, m. p. 141—142°, stable, but by boiling in xylene, the (*s*)-isomeride produced, and by distillation under reduced pressure (13 mm.) this is also produced (b. p. 253—254°/13 mm.); (*s*)-2-m-*nitrobenzoylindazole*, stout, white crystals (benzene), needles (ether), m. p. 134°; (*l*)-2-m-*nitrobenzoylindazole*, very unstable; crystallisation from methyl alcohol hydrolyses the product; pale green, m. p. 142—144° (impure); (*s*)-2-p-*nitrobenzoylindazole*, fine needles, m. p. 164—165°; (*l*)-2-p-*nitrobenzoylindazole*, greenish-yellow, m. p. 137—138°, long heating giving the (*s*)-form; (*s*)-5-*bromo*-2-o-*nitrobenzoylindazole*, prisms, m. p. 186—187°; (*l*)-5-*bromo*-2-o-*nitrobenzoylindazole*, greenish-yellow needles, m. p. 189°, fairly stable, but slowly changed to the (*s*)-isomeride by heat; (*s*)-2-o-*chlorobenzoylindazole*, small prisms, m. p. 99°; (*l*)-2-o-*chlorobenzoylindazole*, fine, pale yellow needles, m. p. 76—77°, fairly stable; (*s*)-2-*phenylacetylindazole*, flat needles, m. p. 67—68°; (*l*)-2-*phenylacetylindazole*, m. p. 106—107°; (*s*)-2-o-*nitrophenylacetylindazole*, needles, m. p. 124—125°; (*l*)-2-o-*nitrophenylacetylindazole*, small needles, m. p. 107—108°, easily converted to the (*s*)-isomeride; (*s*)-2-*cinnamoylindazole*, fine needles, m. p. 120—121°; (*l*)-2-*cinnamoylindazole*, needles, m. p. 152—156°, not very stable; (*s*)-2-o-*nitrocinnamoylindazole*, fine needles, m. p. 185—187°; (*l*)-2-o-*nitrocinnamoylindazole*, fine, greenish-yellow needles, m. p. 156—157·5°, on heating giving the colourless stable isomeride; 2-*indazolecarboxyl chloride*, from indazole and carbonyl chloride in dry ether at —10° (produced together with di-indazyl carbonate) forms fine needles, m. p. 73—74°. It is decomposed to indazole by warm water, and with methyl alcohol gives *methyl indazole-2-carboxylate*. The *amide*, from ammonia and the above chloride, in ether forms needles, m. p. 167°. The labile form of the acid chloride could not be prepared. The following are also described: (*s*)-2 : 2′-*di-indazyl carbonate*, glassy needles, m. p. 137—138°, is prepared as a by-product of the above reaction and as main product on warming the acid chloride with indazole; (*l*)-2 : 2′-*di-indazyl carbonate*, from silver indazole and the above chloride in dry ether at —10°, is very unstable and has m. p. 149—151°; (*s*)-2-*indazolecarbanilide*, from indazole and phenylcarbimide or from the chloride and aniline, stout crystals, m. p. 104—105°; (*l*)-2-*indazolecarbanilide*, from indazole and phenylcarbimide in dry ether at —15°, crystals, m. p. 105—106°, is converted to the stable isomeride after heating for 2 hours; (*s*)-2 : 2′-*di-indazyl succinate*, small needles, m. p. 159°; (*l*)-2 : 2′-*di-indazyl succinate*, greenish-yellow needles, m. p. 140°, easily converted to the stable isomeride; 2-*indazyl hydrogen succinate*, needles, m. p. 146—147°, is prepared from silver indazole and succinyl chloride in dry ether and hydrolysing the *chloride* so obtained; (*s*)-*2-indazole*-p-*toluenesulphonate*, small, stout crystals; (*l*)-*2-indazole*-p-*toluenesulphonate*, small, six-sided crystals, easily changed to the (*s*)-isomeride; *2-indazyl phenyl carbonate*, from 2-indazolecarboxyl chloride and sodium phenoxide in dry ether, m. p. 91°; *2-indazyl* o-*nitrophenyl carbonate*, waxy needles, m. p. 97—98°, on distillation giving nitrophenylindazole (m. p. 153—154°, b. p. 245°/27 mm.); *2-indazyl* p-*tolyl thiocarbonate*, long needles, m. p. 123°, decomposed on distillation under diminished pressure, giving a *compound*, m. p. 197—199°. 2-*Picrylindazole* from picryl chloride and indazole, golden, rhombic plates, m. p. 208—210°, possesses no basic properties. The refractive indices, rotatory dispersions, and densities are given of the following: (*s*)-*2-acetyl-3-ethylindazole*, $d_4^{51\cdot5}$ 1·0951, $n_{He}^{51\cdot5}$ 1·55639; (*s*)-*2-acetyl-6-methylindazole*, $d_4^{4\cdot95}$ 1·1623, $n_{He}^{4\cdot9}$ 1·58676; (*s*)-*2-propionyl-5-methylindazole*, d_4^{100} 1·0544, n_{He}^{100} 1·53682; (*l*)-*2-propionyl-5-methylindazole*, $d_4^{99\cdot4}$ 1·0505, $n_{He}^{99\cdot4}$ 1·55099.

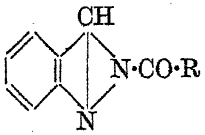
The authors have shown that the presence of negative groups in aliphatic 2-acyl residues precludes the existence of the labile isomeride, but in aromatic acyl residues, with the negative group in the *o*- or *p*-position, the labile form has considerable stability, although if the negative group is in the *m*-position, the labile isomeride is less stable.

Attempts to prepare aminobenzoylindazoles by reduction of the corresponding nitro-compounds were unsuccessful. 2 : 2′-Diindazole derivatives of dibasic acids gave labile forms of varying stability.

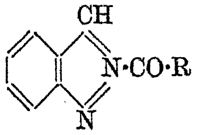
Three possible formulæ are suggested for the acylindazoles:



(*a*)



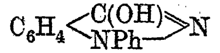
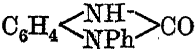
(*b*)



(*c*)

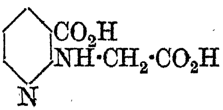
of which (*c*) is not considered seriously.

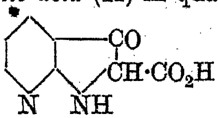
Spectrochemical experiments indicate (*a*) to be unlikely. The authors believe the isomerism to be steric in character and from measurements of the refractive index and rotatory dispersion it appears that formula (*b*) is the most likely for both isomerides. Against this, however, it is urged that the colour of certain of the labile isomerides suggests a quinonoid structure which would indicate (*a*) to be more likely; also that according to formula (*b*) the benzene ring and the 3-ring would not be co-planar, whereas for formula (*a*) the rings are co-planar; in the former case, isomerism would involve a large strain. Also if formula (*a*) be correct, hydrogen chloride should add on to the 1-nitrogen atom with difficulty in the case of one isomeride, owing to the proximity of the acyl group. This has been found to be true, the hydrogen chloride actually splitting off the acyl group. The question is left undecided. A. E. C.

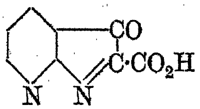
Carbonyldiphenylhydrazine. R. Stollé (*Ber.*, 1924, **57**, [*B*], 1063—1066).—Carbonyldiphenylhydrazine was apparently obtained by Acree (A., 1903, i, 861) from αα-diphenylhydrazine-β-carbonyl chloride. Diphenylcarbamyl azide, m. p. 85° [decomp. $+xC_6H_6$, m. p. 61°; Toschi (A., 1914, i, 740), gives 78—79°] on heating in tetrahydronaphthalene or xylene gives the unsaturated radical, $Ph_2N\cdot CO\cdot N<$, but the carbonyl-diphenylhydrazine which is undoubtedly formed suffers rearrangement to 3-hydroxy-1-phenylbenzpyrazole,  $C_6H_4{<}\substack{C(OH)\\ NPh}{>}N$ (or the corresponding lactam) (cf. Curtius and Schmidt, A., 1923, i, 1080). This substance, dense crystals, m. p. 209°, is converted by methyl sulphate into a mixture of the *N*- and *O*-ethers, the latter forming colourless plates, m. p. 95° (cf. Konig and Reissert, A., 1899, i, 457). In moist tetrahydronaphthalene, diphenylcarbamylazide yields tetraphenylcarbazide, $(NPh_2\cdot NH)_2CO$. Ethyl ββ-diphenylhydrazinoformate, m. p. 141°, is obtained as a by-product when diphenylcarbamylazide is crystallised from alcohol. The action of carbonyl chloride on *o*-aminodiphenylamine yields *sym-di-*o : o′*-anilinodiphenylcarbamide*, m. p. 204°, and a small quantity of a *substance*, m. p. 160°, containing chlorine which with alkali or pyridine yields the above carbamide. The insensitiveness of diphenylcarbamylazide towards water, acids, and alkalis leads to the consideration of the phenylbenziminazolone formula,  $C_6H_4{<}\substack{NH\\ NPh}{>}CO$. The experiments to prepare carbonylhydrazines and benzpyrazolones are being continued. R. B.

Condensation of 2-Aminonicotinic Acid with Chloroacetic Acid to Derivatives of 1 : 7-Benzdiazole. E. Sucharda (*Roczniki Chemji*, 1923, **3**, 236—250).—So far no compounds analogous to indole or indigotin have been prepared containing pyridine in place of benzene rings. The synthesis of such compounds is now described.

2-Aminonicotinic acid (Phillips, A., 1894, i, 301) condenses with chloroacetic acid in the presence of potassium carbonate to give a good yield of *pyridylglycinecarboxylic* acid (I) crystallising with $1H_2O$ and melting in the anhydrous condition at 218—219° (decomp.) with previous shrinking; the substance is strongly acid and forms a *sodium* salt, grey needles, $C_8H_7O_4N_2Na,3H_2O$. The action of mineral acids on the acid (I) leads to 3-*keto*-2 : 3-*dihydro*-1 : 7-*benzdiazole-2-carboxylic acid* (II) in quantitative yield.


(I.)


(II.)


(III.)

The new acid forms yellow crystals containing $1H_2O$ which is lost at 120°, the anhydrous substance melting at 220° (decomp.) with previous darkening; it is amphoteric in nature, the basic character predominating. The *hydrochloride* forms yellow needles, m. p. 284° (decomp.); the *sulphate*, $(C_8H_6O_3N_2)_2,H_2SO_4,4H_2O$, forms yellow crystals, m. p. 225° (decomp.). By the action of sodium nitrate on the above sulphate the 1-*nitroso* derivative of the acid is produced; it is a microcrystalline, flesh-coloured substance decomposing violently at 250—260°, strongly acid in character, giving no compounds with mineral acids and dissolving in alkalis with a red colour. When heated with dilute sulphuric acid in a sealed tube the nitroso-compound gives 2-hydroxynicotinic acid, whilst the action of the concentrated reagent in an open vessel leads to 2-aminonicotinic acid. When the acid (II) is oxidised in ammoniacal solution with potassium ferricyanide or permanganate, the *dehydro* compound (III) is obtained, forming small, red needles, m. p. 259—260° (decomp.). The compound shows a fine violet-red colour in solution and dyes wool from an acid bath. It readily undergoes reduction. The dehydro-compound is also obtained by the action of atmospheric oxygen on solutions of the acid (II) in ammonia, but not in potassium or sodium hydroxides.

It is pointed out that the acid (I) differs from phenylglycine carboxylic acid by the greater stability of the carboxyl group in position 3 and the more ready formation of the indole derivative (II), whilst the latter shows characteristic behaviour on oxidation.

G. A. R. K.

Hydroxylamine, Hydrazine, and their Derivatives as "Oxidising Agents" in the Formation of Induline. K. A. HOFMANN, F. HARTMANN, and F. KROLL (*Ber.*, 1924, **57**, [*B*], 945—963).—The formation of indulines of the benzene and naphthalene series from aniline and α-naphthylamine occurs, not only with typical oxidising agents, such as oxygen, but also with compounds of nitrogen which are generally placed among the strongest reducing agents, such as hydroxylamine, phenylhydroxylamine, hydrazobenzene, phenylhydrazine, and hydrazine. The latter substances are constrained by the energy conditions of ammonium salt formation to withdraw hydrogen from aniline and α-naphthylamine, thus leading to oxidation and production of indulines.

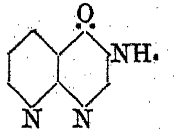
H. W.

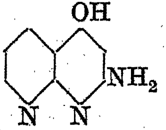
Derivatives of Mono- and Di-substituted Hydrazodithiocarbonamides. E. FROMM and P. JOKL (*Monatsh.*, 1924, **44**, 298—305; cf. Fromm, Nerz, and Layer, A., 1923, i, 1239).—Monophenylhydrazodithiodicarboxylamide on boiling with 10% hydrazine hydrate solution and acidifying, yielded a mixture of 2-amino-5-thiol-1-phenyl-1 : 3 : 4-triazole, and 2 : 5-dithiol-1-phenyl-1 : 3 : 4-triazole (cf. Arndt, A., 1922, i, 375). The former substance yielded an *acetyl* derivative, m. p. 187°. The dithioltriazole was converted by methyl sulphate and ammonia into 2 : 5-dimethylthiol-1-phenyl-1 : 3 : 4-triazole, which was oxidised cautiously by permanganate to 2 : 5-*dimethylsulphonyl*-1-*phenyl*-1 : 3 : 4-*triazole*, m. p. 218°, the latter, when hydrolysed by alkali, giving 2-*hydroxy*-5-*methylsulphonyl*-1-*phenyl*-1 : 3 : 4-*triazole*, white prisms, m. p. 221°. 2 : 5-Dithiol-1-phenyltriazole gives with benzyl chloride and sodium ethoxide 2 : 5-*dibenzylthiol*-1-*phenyl*-1 : 3 : 4-*triazole*, m. p. 110°.

Diallylhydrazodithiodicarboxylamide when heated with hydrazine hydrate is converted into allylamine and 2 : 5-*dithiol*-1-*allyl*-1 : 3 : 4-*triazole*, m. p. 148° (*lead* derivative, $C_5H_5N S_2Pb$, decomp. 290°; *mercury* derivative, $C_5H_5N_3S_2Hg$, m. p. 188°, decomp. 280°). The allyltriazole is oxidised by bromine water to the *polysulphide*, $(C_5H_5N_3S_2)_n$, yellow crystals, m. p. 175°. Monoallylhydrazodithiodicarboxylamide when heated with 10% hydrazine hydrate solution yields 1-*amino*-2-*allylamino*-5-*thiol*-1 : 3 : 4-*triazole*, white prisms, m. p. 202° (*benzylidene* derivative, m. p. 204°). Monophenylhydrazodithiodicarboxylamide when oxidised by cold alkaline hydrogen peroxide affords 2-*amino*-5-*phenylamino*-1 : 3 : 4-*thiodiazole*, m. p. 205°, which forms a *benzylidene* derivative, yellow needles, m. p. 238°, a *benzoyl* derivative, m. p. 278°, and with acetic anhydride affords 2-*diacetamido*-5-*phenylamino*-1 : 3 : 4-*thiodiazole*, m. p. 264°. Monophenylhydrazodithiodicarboxylamide on treatment with hydrochloric acid in glacial acetic acid yields 2-*acetamido*-5-*thiol*-1 : 3 : 4-*thiodiazole*, m. p. 282°, which when treated with benzyl chloride and sodium ethoxide, gives 2-*acetamido*-5-*benzylthiol*-1 : 3 : 4-*thiodiazole*, m. p. 164°; the compound of m. p. 282° forms a *lead* derivative, $C_8H_8O_2N_6S_4Pb$, decomp. 250°, and with acetic anhydride yields 2-*diacetamido*-5-*thiol*-1 : 3 : 4-*thiodiazole*, m. p. 202°. F. A. M.

Derivatives of 1 : 3 : 8-Benztriazine and the Preparation of 2-Aminonicotinic Anhydride. L. KLISIECKI and E. SUCHARDA (*Roczniki Chemji*, 1923, 3, 251—260).—2-Aminonicotinic acid behaves in a manner analogous to that of anthranilic acid and condenses with formamide and acetamide, although the yield of condensation product is small. Thus on heating with formamide it yields 4-*hydroxy*-1 : 3 : 8-*benztriazine* (I), sparingly soluble, colourless prisms which do not melt at 385° (*hydrochloride*, colourless crystals). The 2-*methyl* derivative is obtained by substituting acetamide for formamide in the original condensation and forms colourless needles, m. p. 258°; the *hydrochloride* is somewhat sparingly soluble and was obtained in colourless needles. In contrast to the parent substance, the methyl derivative is readily soluble in water, etc., as well as in mineral acids and alkalis. This difference is accounted for by assuming the methyl derivative to have a lactim and the parent substance a lactam structure.

(I.)





(II.)

The alternative structure (II) is disproved because the substance does not show any of the characteristic reactions of the primary amino group. Moreover, the more acid nature of the above methyl derivative is shown by the fact that the chlorine in the hydrochloride cannot be estimated by direct titration as in the case of (I).

An attempt to condense methyl 2-aminonicotinate with ethyl acetate by means of sodium failed, the product forming colourless prisms, m. p. 378° (decomp.); on acid or alkaline hydrolysis, it reverts to 2-aminonicotinic acid, of which it appears to be the *anhydride*, probably of the formula $C_{12}H_8O_2N_4$. G. A. R. K.

Amine Oxidation. IX. Hydrazyls. S. Goldschmidt (*Annalen*, 1924, **437**, 194—226; cf. A., 1920, i, 257; 1922, i, 475, 476).—A further series of investigations on different types of hydrazyls has revealed equilibrium conditions which do not conform to the Thiele-Werner principle, and the regularities observed by Wieland in the dissociation of tetra-arylhydrazines (A., 1911, i, 567; 1912, i, 904) do not hold for the substituted hydrazyls. The tetrazans of the α-acyl-α-β-diarylhydrazyls,

$$Ar(R\cdot CO)N\cdot N\cdot Ar\ .\ .\ .$$

are much less dissociated than the hexa-aryltetrazans, and the following order is given: αα′-diacetyl-αβα′β′-tetraphenyltetrazan < α′α-dibenzoyl-αβα′β′-tetraphenyltetrazan < αα′-diacetyl-αβα′β′-tetratolyltetrazan < αα′-dibenzoyl-αβα′β′-tetratolyltetrazan. Dissociation of the tetrazan is thus weakened when the phenyl group is replaced by tolyl, and the αα′-diacetyl-αβα′β′-tetra(*m*-dimethylaminophenyl)tetrazan is almost completely dissociated into the hydrazyl. A further study of the effect of different acyl groups on the dissociation of diacyl-αα′ββ′-tetraphenyltetrazan, based on the reaction with αα-diphenyl-β-trinitrophenylhydrazine:

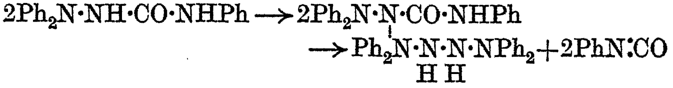
$$Ph_2N\cdot NH\cdot C_6H_2(NO_2)_3+R\cdot CO\cdot NPh\cdot NPh\ .\ .\ .$$
$$\rightleftharpoons Ph_2N\cdot N\cdot C_6H_2(NO_2)_3\ .\ .\ .+R\cdot CO\cdot NPh\cdot NHPh,$$

showed that the dissociation did not depend on the dissociation constant of the acid, nor was a simple connexion observed between the solubility of the tetrazan and its degree of dissociation. The β-acyl-αα-diarylhydrazyls readily decomposed, and their behaviour was therefore studied in solution. Equilibrium between the hydrazyl and the tetrazan is a definite time reaction. The free hydrazyl reacts instantly with quinol: $2R_2N\cdot NR'\ .\ .\ .+C_6H_4(OH)_2 \longrightarrow 2R_2N\cdot NHR'+C_6H_4O_2$, the solution being decolorised. The red colour, however, at once begins to reappear as the tetrazan dissociates, and the velocity of the dissociation increases greatly with the temperature, but decreases with dilution. The dissociation is also dependent on the nature of the solvent, and in the case of the tetrazan obtained from diphenylacetylhydrazine it was found that the dissociation and the solubility of the tetrazan are roughly proportional. With the dibenzoyltetrazans, the dissociation corresponds with Ostwald's dilution law. Confirmation of these results was obtained by a colorimetric method. Two formulæ are discussed for the acyl-αα-diarylhydrazyls, but in the absence of any satisfactory criteria for bivalent nitrogen and univalent oxygen, and in the absence also of evidence to the contrary, preference is given to the formula $R_2N\cdot\underset{|}{N}\cdot CO\cdot R$ previously used.

The behaviour of carbonic acid derivatives on oxidation has also been studied. Tetraphenylsemicarbazide and diphenyldimethylsemicarbazide yield deep blue solutions, which react at once (with decolorisation) with nitrogen dioxide, bromine, and triphenylmethyl. By the reaction with quinol these solutions are shown to contain the radicals $Ph_2N{\cdot}\underset{|}{N}{\cdot}CO{\cdot}NH{\cdot}NPh_2$ and

$$PhMe{\cdot}N{\cdot}\underset{|}{N}{\cdot}CO{\cdot}NH{\cdot}NPhMe,$$

respectively. Both radicals are completely unimolecular in solution and at —70° obey Beer's law. They are distinguished by their reactivity towards hydrogen. The dimethyldehydro compound reacts quantitatively with quinol whilst only the tetraphenyldehydrocarbazide was isolated in the free state by the reaction with trinitrophenylhydrazyl. The dehydrogenation of the second nitrogen in the carbazide is probably possible although with difficulty, but the formation of hydrazyls from the corresponding urethane, $RR'N{\cdot}NH{\cdot}CO_2Et$, or chloride, $RR'N{\cdot}NH{\cdot}CO{\cdot}Cl$, was not observed. Triphenylsemicarbazide, $Ph_2N{\cdot}NH{\cdot}CO{\cdot}NHPh$, on oxidation with lead peroxide in benzene solution, leads exclusively to tetraphenyltetrazan,



$$2Ph_2N{\cdot}NH{\cdot}CO{\cdot}NHPh \longrightarrow 2Ph_2N{\cdot}\underset{|}{N}{\cdot}CO{\cdot}NHPh \longrightarrow Ph_2N{\cdot}\underset{H}{N}{\cdot}\underset{H}{N}{\cdot}NPh_2 + 2PhN{:}CO$$

Experiments on the oxidation of alkylarylhydrazines showed that the presence of the alkyl group diminished the capacity for oxidation of the hydrazine, and the expected alkyl-substituted hydrazyls were not obtained. By condensation of triphenylchloromethane with diphenylhydrazine, αα-diphenyl-β-triphenylmethylhydrazine, $Ph_2N{\cdot}NH{\cdot}CPh_3$, was obtained, which on oxidation loses hydrogen, probably yielding the unsaturated radical, $Ph_2N{\cdot}\underset{|}{N}CPh_3$, which at once gives triphenylcarbinol and tetraphenyltetrazan. The condensation of triphenylchloromethane with hydrazobenzene yielded similarly αβ-diphenyl-α-triphenylmethylhydrazine,

$$CPh_3{\cdot}NPh{\cdot}NHPh,$$

which on oxidation yielded triphenylcarbinol and azobenzene. It is probable therefore that exchange of an aryl group for alkyl renders the hydrazyls too unstable to exist.

A comparison of the known hydrazyls indicates that the nitrogen atom in the tertiary hydrazines possesses no basic properties and that the hydrogen atom attached to it is acidic. This appears to be a fundamental condition for the formation of hydrazyls.

[With A. Wolf.]—*αα'-Diphenyl-*ββ-p-*chlorophenylhydrazine*, prismatic needles, m. p. 114—116° (decomp.), obtained by the action of ethyl hypochlorite on triphenylhydrazine at —80° in ethereal solution, yields *p*-chloroaniline on reduction. Oxidation with lead peroxide in methyl ether at —70° yields *αα-diphenyl-*p-*chlorophenylhydrazyl*, a deep blue solution which obeys Beer's law at —20°, but not at —70°.

[With I. Drimmer.]—Chloroacetyl chloride and hydrazobenzene in ethereal solution give *α-chloroacetyl-*αβ-*diphenylhydrazine*, $(CH_2Cl{\cdot}CO)NR{\cdot}NHPh$, plates, m. p. 163° (decomp.), which on oxidation with lead peroxide in benzene yield *αα'-dichloroacetyl-*αβα'β'-*tetraphenyltetrazan*, yellow prisms, m. p. 111—112° (decomp.). Similarly, from dichloroacetyl chloride is obtained *α-dichloro-*

acetyl-αβ-diphenylhydrazine, m. p. 134°, and on oxidation, *αα′-di-dichloroacetyl-αβα′β′-tetraphenyltetrazan*, m. p. 102—104° (decomp.). *α-Propionyl-αβ-diphenylhydrazine*, tablets, m. p. 140·5°, on oxidation yields *αα′-propionyl-αβα′β′-tetraphenyltetrazan*, yellow rhomboids, m. p. 117° (decomp.).

[With R. Wagner.]—αβ-Bis-*m*-dimethylaminophenylhydrazine with acetic anhydride is converted into α-acetyl-αβ-bis-*m*-dimethylaminophenylhydrazine, needles, m. p. 123°, which on oxidation with lead peroxide in chloroform solution at —20° yields a deep blue solution of the *hydrazyl*.

[With E. Wolffhardt.]—β-Acetyl-αα-diphenylhydrazine, obtained by acetylation of αα-diphenylhydrazine (Fischer, A., 1878, 190) on oxidation with lead peroxide in acetone solution, yields *ββ′-diacetyl-ααα′α′-tetraphenyltetrazan*, prismatic plates, m. p. 141° (decomp.), which on reduction with quinol yield the original hydrazine (m. p. 185°). With triphenylmethyl in chloroform solution the tetrazan yields triphenylmethyl peroxide and a *substance*, $C_{33}H_{28}ON_2$, dense crystals, melting at 159° to a red liquid, which on boiling with acetic acid yields triphenylcarbinol and acetyldiphenylhydrazine. In benzene solution a *substance*, $C_{33}H_{28}ON_2$, was obtained, darkening at 250°, m. p. 256°. β-Benzoyl-αα-diphenylhydrazine on oxidation with potassium ferricyanide in alcoholic solution yields the *β-benzoyl-αα-diphenylhydrazyl*, deep blue solutions, reconverted to hydrazine with quinol. *β-Anisoyl-αα-diphenylhydrazine* (from anisoyl chloride and diphenylhydrazine), m. p. 217°, on rapid treatment with sodium ethoxide in alcoholic solution is converted into the tetrazan, the original anisoyl hydrazine being very readily reprecipitated. β-o-*Nitrobenzoyl-αα-diphenylhydrazine*, citron-yellow needles, m. p. 203°, β-m-*nitrobenzoyl-αα-diphenylhydrazine*, yellowish-green needles, m. p. 205°, and β-p-*nitrobenzoyl-αα-diphenylhydrazine*, orange-yellow needles, m. p. 206°, are similarly prepared. The *o*-nitrobenzoylhydrazine on oxidation in toluene solution yields the *tetrazan*, bright yellow crystals rapidly changing to violet in the light.

[With A. Wolf.]—On oxidation with lead peroxide in a mixture of tetrachloroethane and toluene, tetraphenylcarbazide yields a deep blue solution stable at —25° but rapidly decomposing at the ordinary temperature. The N-*dehydrotetraphenylcarbazide* is isolated by the addition of αα-diphenyltrinitrophenylhydrazyl, the product, after washing from diphenyltrinitrophenylhydrazine with toluene, giving a dark violet solution in chloroform. Diphenyldimethylcarbazide on oxidation in chloroform–ether solution similarly yields a deep lavender-blue solution, from which the N-*dehydrodiphenyldimethylcarbazide* may be isolated as in the case of triphenylhydrazyl.

[With S. Nathan.]—Triphenylchloromethane and αα-diphenylhydrazine in benzene solution yield *αα-diphenyl-β-triphenylmethylhydrazine*, m. p. 136—137° (turning brown at 126°), which on oxidation with lead peroxide in benzene solution yields tetraphenyltetrazene and triphenylcarbinol. Similarly, triphenylmethyl chloride and αβ-diphenylhydrazine in ethereal solution give *αβ-diphenyl-α-triphenylmethylhydrazine*, prismatic plates, m. p. 107°, which is converted into triphenylcarbinol and azobenzene on oxidation with lead peroxide in alcoholic solution. *αα-Dibenzyl-β-*tert.*-butylhydrazine*, rhombic plates, m. p. 85°, from αα-dibenzylhydrazine and *tert.*-butyl bromide, yields only the unchanged hydrazine on oxidation. *αα-Dibenzyl-β-trinitrophenylhydrazine*, m. p. 176°, similarly prepared from picryl chloride, on oxidation yields trinitrophenylbenzylidenehydrazine, m. p. 262° (cf. Curtius and Dedichen, A., 1895, i, 29). α-Phenyl-β-trinitrophenyl-α-methylhydrazine on oxidation in chloroform solution at —70° yields a transient, dark violet solution, becoming yellowish-brown. At room temperature, oxidation yields a *substance*, $C_{26}H_{18}O_9N_{10}$, yellowish-red, rhombic crystals, m. p. 150°. R. B.

Halogenated Aromatic Hydrazines. I. 3 : 4-Dibromophenylhydrazine. E. VOTOČEK and P. JIRŮ (*Chem. Listy*, 1924, **18**, 113—117).—The 3 : 4-dibromophenylhydrazine prepared by Meyer (A., 1893, i, 155) by the bromination of acetone phenylhydrazone is shown to be the *p*-monobromo compound. The dibromo compound has now been prepared by reducing diazotised 3 : 4-dibromoaniline with stannous chloride; it forms fairly stable, yellow needles, m. p. 75°. It forms a *hydrochloride*, decomp. 215°, a *sulphate*, needles, decomp. 180°, an *oxalate*, decomp. 162—163°, and a *picrate*, decomp. 154—156°. The *acetyl* derivative forms red needles, m. p. 181—182°. The base forms *hydrazones* with the following compounds: benzaldehyde, yellow crystals, m. p. 128°; salicylaldehyde, reddish-yellow crystals, m. p. 190°; acetone, an oil; arabinose, a solid difficult to purify, decomp. 82—83°; rhamnose, m. p. 153—154°; dextrose, colourless crystals, m. p. 165—167°, and a colourless *compound*, m. p. 70°, containing less bromine; the compounds obtained from lævulose and galactose could not be obtained pure. The *osazone* prepared from dextrose or lævulose and the hydrochloride of the base forms yellow crystals, m. p. 225—226° (decomp.).

It is shown that both 3 : 4- and 2 : 4-dibromophenylhydrazine and also the *p*-bromophenylhydrazine obtained by Meyer give *p*-bromoaniline on reduction with zinc and hydrochloric acid.

G. A. R. K.

Preparation of *p*-Dialkylaminoarylphosphinous Acids. L. CASSELLA & Co., G.M.B.H. (Brit. Pat. 214836).—Phosphorus trichloride is heated with an excess of a dialkylarylamine and the resulting arylphosphorus chloride is converted into the *p*-dialkylaminoarylphosphinous acid or a salt of the same in the usual way (*e.g.*, with sodium hydroxide). The reaction is smooth and almost quantitative, and the products, which possess therapeutic properties, are of a high degree of purity. Details are given for the preparation of sodium 1-dimethylamino-4-phenylphosphinite, colourless needles ($+2H_2O$). Sodium 1-dimethylamino-4-phenyl-3-methylphosphinite forms scales, needles, or prisms ($+3H_2O$). Sodium 1-diethylamino-4-phenyl-3-methylphosphinite forms prisms ($+3H_2O$). Other salts of these acids are also described. W. T. K. B.

Compounds of the Diethylarsine Series. N. I. WIGREN (*Annalen*, 1924, **437**, 285—296).—Dehn's method (A., 1906, i, 150) failed for the diethylarsine series but *iododiethylarsine* (a yellow, irritating liquid, b. p. 70—71°/10 mm.) was prepared from diiodoethylarsine by Auger's method, as modified by McKenzie and Wood (T., 1920, **117**, 406). Oxidation of iododiethylarsine by hydrogen peroxide gives a diethylarsinic acid possessing properties sharply distinguished from those of the (probably impure) diethylarsinic acid described by Landolt (*J. pr. Chem.*, 1854, **63**, 283). It gives no precipitate with silver, ferric, lead, or copper salt solutions, whilst the acid barium salt described by Landolt could not be obtained. The behaviour of diethylarsine and bisdiethylarsineoxide (below) with mercuric chloride in hydrochloric acid shows that, contrary to the assumptions of Biginelli (A., 1901, i, 20) and Klason (A., 1915, i, 486), neither of these compounds can be the volatile arsenic compound produced by different arsenic moulds. The above iodo compound is converted by alkali into *bisdiethylarsineoxide*, $(AsEt_2)_2O$, a colourless, highly refracting liquid, b. p. 97—98°/10 mm., which has an unbearable, irritating odour, and oxidises to diethylarsinic acid in the air. Reduction of iododiethylarsine with zinc copper couple and alcohol (cf. Palmer, A., 1894, i, 400) in a specially designed apparatus affords *diethylarsine*, a colourless liquid, b. p. 105°, which undergoes spontaneous oxidation in air and has a garlic odour. With Biginelli's solution, it yields lustrous needles of the *mercurosochloride*, $AsEt_2Cl,2HgCl$, this, with boiling water, yielding chlorodiethylarsine. Diethylarsinic acid, colourless needles, m. p. 133—134° (Landolt gives 190°), forms a soluble *silver* salt (needles), and a *nitrate*, Et_2AsO_2H,HNO_3, prisms, m. p. 71—72°. The constants for the acid (by the methyl acetate, and Sörensen's indicator method [A., 1909, i, 861]) are $K_b=3{\cdot}7\times10^{-13}$. $K_a=3{\cdot}0\times10^{-7}$. R. B.

3-Amino-4 : 4′-dihydroxyarsenobenzene, and its N-Methylenesulphinate and N-Methylenesulphonate Derivatives. M. C. HART and W. B. PAYNE (*J. Amer. Pharm. Assoc.*, 1923, **12**, 688—695).—The preparation of 3-amino-4 : 4′-dihydroxyarsenobenzene and the determination of its toxicity are described, together with similar experiments with the (unstable) sodium *N*-methylenesulphinate and (more stable) sodium *N*-methylenesulphonate. The reduction with sodium hyposulphite of an equimolecular mixture of the two arsinic acids is not a general method for the production of unsymmetrical derivatives.

The loss of one of the essential anchoring groups from salvarsan does not impair its therapeutic efficiency.

CHEMICAL ABSTRACTS.

3-Amino-4-hydroxyarsenophenyl-4′-glycine and its N-Methylenesulphinate and N-Methylenesulphonate Derivatives. M. C. HART and W. B. PAYNE (*J. Amer. Pharm. Assoc.*, 1923, **12**, 759—768).—The toxic and maximum tolerated doses of 3-amino-4-hydroxyarsenophenyl-4′-glycine and its *N*-methylenesulphonate and *N*-methylenesulphinate have been determined;

the toxicity and trypanocidal activity decrease in the order given. The effect of the introduction of these groups (yielding soluble compounds) on the therapeutic activity is parallel to that in the case of salvarsan. Although these compounds are as effective therapeutically as the corresponding compounds of the salvarsan series, they are deficient in some of the essential anchoring groups considered by Ehrlich to be necessary for the highest type of therapeutic efficiency claimed to have been reached in salvarsan.

CHEMICAL ABSTRACTS.

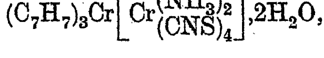
Aromatic Selenonic Acids. II. *m*-Xyleneselenonic Acid. R. ANSCHÜTZ and F. TEUTENBERG (*Ber.*, 1924, **57**, [*B*], 1018—1023; cf. A., 1919, i, 24).—By the action of selenic acid on *m*-xylene in the presence of acetic anhydride a crystalline *m*-xylene-4(?)-selenonic acid, m. p. 130—130·5°, is obtained which presents analogies with *m*-xylene-4-sulphonic acid, but the position of the selenonic group has not been definitely determined. Fractional crystallisation gave no indication of the formation of the two possible isomerides. The yield, one of 75%, could not be improved, since concentration of the mother-liquor in a vacuum led to an explosion. *m*-Xylene-4-selenonic acid is stable towards boiling sodium hydroxide, is not attacked by hydrogen peroxide, and forms a *dihydrate*,

$$C_6H_3Me_2{\cdot}SeO_3H,2H_2O,$$

similar *dihydrates* of the *o*- and *p*-xylene-4-selenonic acids being described. The *o*-, *m*-, and *p*-xylene-4-sulphonic acids also yield dihydrates. The *salts* of 10 metals and *m*-xylene-4-selenonic acid are described, and the corresponding *m*-xylene-4-sulphonates, most of which are new (cf. Jacobsen, *Ber.*, 1878, **11**, 18), particular attention being directed to the number of molecules of water of crystallisation.

R. B.

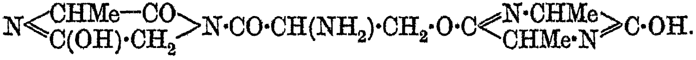
Organo-chromium Compounds. V. Chromium Tolyl Compounds. F. HEIN and R. SPAETE (*Ber.*, 1924, **57**, [*B*], 899—908; cf. A., 1921, i, 826; 1922, i, 76, 77; this vol., i, 437).—The action of an ethereal solution of magnesium *p*-tolyl bromide on chromium chloride yields a mixture of chromium polyphenyl bromides from which the following substances are derived by methods which are somewhat modified from those used previously (*loc. cit.*): *chromiumpenta*-p-*tolyl carbonate*, $[Cr(C_7H_7)_5]_2CO_3,6H_2O$, orange crystals, m. p. 139—140°, and the corresponding tetrahydrate; the additive *compound* of chromiumpenta-*p*-tolyl bromide and mercuric chloride; *chromiumpenta*-p-*tolyl hydrogen anthranilate*, $2NH_2{\cdot}C_6H_4{\cdot}CO_2Cr(C_7H_7)_5,NH_2{\cdot}C_6H_4{\cdot}CO_2H$, m. p. 170° after previous softening; *chromiumtetra*-p-*tolyl hydrogen anthranilate*, $NH_2{\cdot}C_6H_4{\cdot}CO_2Cr(C_7H_7)_4,NH_2{\cdot}C_6H_4{\cdot}CO_2H$, m. p. 176° after previous softening; *chromiumtri*-p-*tolyl hydroxide*, *chromiumtri*-p-*tolyl iodide*, $2Cr(C_7H_7)_3I,Et_2O$, m. p. 115—119° (decomp.); *chromiumtri*-p-*tolyl hydrogen anthranilate*, an orange-yellow, amorphous substance, m. p. 145—149°; *chromiumtri*-p-*tolyl picrolonate*; *chromiumtri*-p-*tolylchromitetrathiocyanotodiammine*,



$$(C_7H_7)_3Cr\left[Cr\genfrac{}{}{0pt}{}{(NH_3)_2}{(CNS)_4}\right],2H_2O,$$

an unstable, amorphous substance. The *p*-tolyl compounds are all considerably less stable than the corresponding phenyl derivatives, and this difference is even more noticeable with the *o*-tolyl compounds, of which *chromiumtetra*-o-*tolyl hydrogen anthranilate*, m. p. 75—110°, and *chromiumpenta*-o-*tolyl hydrogen anthranilate*, $C_{91}H_{89}O_6N_3Cr_2$, m. p. 151° (decomp.), are described. H. W.

Structure of the Protein Molecule. E. Abderhalden and E. Komm (*Z. physiol. Chem.*, 1924, **136**, 134—146).—When proteins are subjected to progressive partial hydrolysis with dilute hydrochloric acid or water alone at 150—160° for 7 hours, the greater part goes into solution. If the hydrolysate be then evaporated to dryness and the residue mixed with sand and extracted successively with ethyl acetate, chloroform, acetone, and methyl alcohol, it yields characteristic crystalline compounds having an anhydride structure, which can be readily isolated in the pure condition. They are optically inactive and do not give the ninhydrin reaction, indicating the absence of free amino and carboxyl groups. Regarding these compounds as fragments of the original protein molecule, it is concluded that in the protein molecule in addition to the polypeptide chains, anhydride-like residues having the diketopiperazine structure are also present. It is conceivable that these diketopiperazine residues are capable of existing in tautomeric forms, $-NH\cdot CO- \longrightarrow -N{:}C(OH)-$, and the changes in the physico-chemical properties of proteins accompanying denaturation may be in part ascribed to this cause. When silk fibroin is hydrolysed with 0·5% hydrochloric acid as mentioned above, only a very small quantity of it is dissolved, but if the residue be then hydrolysed under the same conditions with four times its quantity of 2% hydrochloric acid it goes completely into solution. The first hydrolysate yields on extraction with ethyl acetate an *anhydride* containing (1 mol. of serine+1 mol. of glycine+3 mols. of alanine, *less* $5H_2O$). It forms needles, m. p. 213—215° (subl.). On treatment with alkali one-fourth of the total nitrogen appears as amino-nitrogen, and from this and other considerations the following structure is suggested:



$$\mathrm{N}{<}\begin{matrix}\mathrm{CHMe{-}CO}\\ \mathrm{C(OH)\cdot CH_2}\end{matrix}{>}\mathrm{N\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot O\cdot C}{<}\begin{matrix}\mathrm{N\cdot CHMe}\\ \mathrm{CHMe\cdot N}\end{matrix}{>}\mathrm{C\cdot OH}.$$

The residue from the above and the second hydrolysate on extraction with chloroform yield alanylglycine anhydride, m. p. 236°. The acetone and methyl alcohol extracts did not yield any characteristic products. Blood proteins on heating with water under pressure are completely dissolved and the hydrolysate on appropriate extraction yields leucine-imide, *iso*leucyl-leucine anhydride, and leucylglycine anhydride. D. R. N.

Reductive Decomposition of Proteins and Toxicity of their Decomposition Products. V. N. Troensegaard (*Z. physiol. Chem.*, 1924, **134**, 100—112; cf. A., 1923, i, 615, 1243; this vol., i, 581).—Acetylated or methylated proteins (casein or gliadin) are reduced, hydrolysed, and fractionated as previously described. The basic fractions show marked toxic properties when injected into guinea-pigs. For the preparation of these hydrated protein derivatives in addition to the methods previously described, acetylgliadin or acetylgelatin may be hydrogenated with magnesium in acetic acid solution and acetylcasein with zinc dust in acetic acid.

W. O. K.

Oxidative and Reductive Scission of Proteins. S. Edlbacher (*Z. physiol. Chem.*, 1924, **134**, 129—139).—Oxyprotosulphonic acid formed from casein by the action of potassium permanganate contains, as compared with casein, about 10% more humin nitrogen and about 10% less monoamino-nitrogen. After oxyprotosulphonic acid is hydrolysed by trypsin, the ratio of the number of methyl groups introduced by methyl sulphate to the formol titration number is the same as before hydrolysis. Further oxidation by hydrogen peroxide results in the formation of "*apo*casein," in which deep-seated changes, as shown by the distribution of nitrogen, have taken place. "*apo*Gelatin," "*apo*arachin," and "*apo*clupein" are also described.

[With K. Erbach.]—The results of Troensegaard on the methylation, reduction, and subsequent hydrolysis of casein are confirmed (cf. preceding abstract). W. O. K.

Structure of the Protein Molecule. E. Abderhalden and E. Komm (*Z. physiol. Chem.*, 1924, **134**, 113—120; 121—128).—(I) From hog's bristles, hydrolysed in an autoclave with double their weight of 2% hydrochloric acid at 120° for 10 hours, the following compounds have been isolated, using the methods previously described (cf. this vol., i, 227): *Di(hydroxyprolyl)glycine anhydride*, $C_{12}H_{17}O_5N_3$, m. p. 174°, $[\alpha]_D^{22}$ —31·65° in alcohol; *iso-leucyl-leucine anhydride*, m. p. 273—277°, $[\alpha]_D^{20}$ —15·96° in aqueous solution, and a product, m. p. 205—210°, possibly impure alanylglycine anhydride. From the proteins of blood, heated for 7 hours in an autoclave at 180° at 10 atm. pressure, the following products have been obtained: *leucylserine anhydride*, m. p. 201—204°, $[\alpha]_D^{20}$ +0·87° (in methyl-alcoholic solution), leucyl glycine anhydride, m. p. 233°, $[\alpha]_D^{20}$ —2·58° in alcoholic solution, and diprolylvaline anhydride, $[\alpha]_D^{20}$ +2·6°.

(II) In order to ascertain whether anhydrides such as are obtained from protein after partial hydrolysis may owe their existence to the conditions of hydrolysis, certain amino-acids and polypeptides have been heated with water for 7 hours at 150°. *l*-Leucylglycyl-*l*-leucine, *dl*-leucyldiglycylglycine, and glycyl-*dl*-leucylglycine, and probably glycyl-*dl*-leucine, yield leucylglycine anhydride. Diglycylcystine yielded no definite product and glycyl-*dl*-tyrosine only the component amino-acids. From the amino-acids, glycine, *d*-alanine, *dl*-leucine, and *l*-tyrosine, after heating with water under the same conditions by themselves or in mixtures, no trace of anhydride could be isolated. W. O. K.

Amide Nitrogen of Caseinogen. J. M. Luck (*Biochem. J.*, 1924, **18**, 679—692).—Only two-thirds of the ammonia liberated by acid hydrolysis of caseinogen is obtained when this protein is submitted even to prolonged tryptic digestion. This undigested residue can be partly precipitated by alcohol and totally precipitated by phosphotungstic acid and alcoholic mercuric chloride. The isolated residue entirely resists tryptic hydrolysis. When it is submitted to acid hydrolysis, glutamic acid and lysine are obtained. Eight to 10% of its total nitrogen occurs as ammonia, which is not associated with the lysine, but is present in amide form. It is concluded that glutamine or a glutamine-containing peptide is present in the tryptic digestion product of caseinogen. The possibility that this compound is a secondary product of enzymic synthesis cannot be excluded. S. S. Z.

Chemistry of Blood Pigments. F. Haurowitz (*Z. physiol. Chem.*, 1924, **136**, 147—159).—A method is described whereby oxyhæmoglobin can be prepared in the crystalline state in considerable quantity from horse-blood (cf. A., 1918, i, 316; 1921, i, 749; 1922, i, 962). The corpuscles are washed thrice by centrifuging with isotonic sodium chloride solution and then dialysed for 2 days against running ice-cold tap water and for 3 days subsequently against distilled water. The corpuscles are then hæmolysed and the dark red liquid is freed from the stroma by centrifuging, cooled with ice, and a current of air is passed through it, when within 10—20 minutes a dark red, crystalline magma begins to separate. The crystals are removed by centrifuging and further freed from moisture on unglazed porcelain tile and brought to 20% moisture content by pressing in a hydraulic press under a pressure of 300 atms. The above operations must be carried through as rapidly as possible as otherwise the product will not crystallise. The needles of oxyhæmoglobin are identical with those obtained by other methods (*loc. cit.*). Hæmoglobin can be readily prepared in a crystalline state without using alcohol by exposing a 40% oxyhæmoglobin paste in a vacuum until complete reduction is effected, when after one or two days it crystallises in hexagonal plates. Crystalline carbon monoxide–hæmoglobin can also be obtained by passing carbon monoxide through oxyhæmoglobin paste and keeping in a cool place. Nitric oxide–hæmoglobin can be prepared by passing nitric oxide free from the higher oxides of nitrogen through a 20% hæmoglobin solution, from which it rapidly crystallises on keeping in the cold. It decomposes on keeping into nitric oxide and hæmoglobin. The so-called water of crystallisation of oxyhæmoglobin preparations obtained by different methods is found to vary between 8·9 and 9·8%. D. R. N.

Biochemistry.

Pharmacology of Cell Respiration. IV. Influence of Temperature on the Spontaneous Oxidation of Hydrocyanic Acid in "Brennorten" ("Combustion Regions") and on the Curve of Oxygen Consumption of Tissues Poisoned by Potassium Cyanide. P. Ellinger (*Z. physiol. Chem.*, 1924, **136**, 19—29).—In the presence of charcoal and a phosphate solution of p_H 7·2, potassium cyanide absorbs oxygen at a rate which, for any given temperature, is proportional to the cyanide concentration. The rate of oxidation increases by 90—100% for a rise in temperature of 10°. A suspension of frog muscle pulp at p_H 7·2 shows an increase in rate of oxidation from 20—30° and a fall from 30—35° which becomes rapid between 35° and 40°, whilst in the presence of various cyanide concentrations frog-muscle shows a minimum rate of oxidation when the concentration of cyanide is 4·5 millimols. per litre at temperatures between 20° and 35°, and when the concentration is 2·25 millimols. at 40°. It is concluded that in addition to inhibiting cell oxidation, potassium cyanide is itself spontaneously oxidised in the tissues (cf. Meyerhof, *Pflüger's Archiv*, 1923, **200**, 1). J. P.

Respiration and Fermentation. H. F. Holden (*Biochem. J.*, 1924, **18**, 536—542).—The " respiration substance " of Meyerhof, obtained by extracting mammalian muscle with boiling water, is destroyed by aëration in contact with washed rabbit, rat, or frog muscle. The alcoholic co-enzyme in yeast or muscle is also destroyed in this way, although it is not readily oxidised by air alone. Neither glutathione nor pancreatic insulin can act as the alcoholic co-enzyme to washed " acetoned " yeast in the presence of potassium phosphate, at a suitable hydrogen-ion concentration at which the natural co-enzyme acts. The " respiration substance " seems to be a collection of irreversibly oxidisable substances, although not in the main lactic acid. A new method of preparation of " acetoned " yeast is described. S. S. Z.

Properties of an alleged Erythropoietic Hormone. C. D. Leake and F. J. Bacon (*J. Pharm. Exp. Ther.*, 1924, **23**, 353—363).—An erythropoietic substance was obtained by extracting with water a mixture of equal parts of desiccated preparations of spleen and red bone-marrow. The activity of the substance was not affected by boiling in aqueous solution or by keeping for long periods in sterile solution, but was destroyed by precipitation with alcohol and ether. The desiccated material, from which the hormone was obtained, contained about 0·24% of water-soluble iron and 2·89% of lecithin-phosphatides. C. R. H.

Spectroscopic Chemical Reactions of some Porphyrins and their Methyl Esters. O. Schumm (*Z. physiol. Chem.*, 1924, **136**, 243—278).—The occurrence of porphyrin (uroporphyrin), kotporphyrin (coproporphyrin), and chloroform-soluble porphyrin is reviewed and an account given of their spectroscopic reactions. Chloroform is not such a suitable solvent for the methyl esters of uroporphyrin and coproporphyrin as is phenol. In this case, the acidity is an important factor, and consequently, different results were shown with different samples of phenol. A phenol–alcohol mixture shows definite differences between the two esters, as does also a pyrrole–alcohol mixture. The latter, however, is unsatisfactory, owing to the brown coloration which develops in the pyrrole itself. Less conclusive results were obtained with toluene, acetone, aniline, and benzene. Carbon tetrachloride, in which the esters are only very slightly soluble, gave definite differences.

The porphyrin prepared from normal fæces differs from both uroporphyrin and coproporphyrin, but is very similar to a preparation made from sulphur–hæmoglobin, and this, in turn, has spectroscopic properties very similar to those of ooporphyrin.

O. O.

Formation of Porphyrin from the Colouring Matter of Blood. O. Schumm and A. Papendieck (*Z. physiol. Chem.*, 1924, **137**, 103—104; cf. this vol., i, 440, and preceding abstract).—In the preparation of a colouring matter allied to porphyrin, by the treatment of oxygen-free blood with hydrochloric acid, the authors have used chloroform to extract the substance from the reaction mixture. The substance thus obtained behaved in a somewhat anomalous manner, and it is now shown that this is probably due to partial esterification during the extraction with chloroform containing some alcohol. The solubility of the porphyrin derivative is greater in such chloroform than in pure chloroform. To avoid esterification, specially purified chloroform should be used. The preparation of the substance under discussion is greatly facilitated by the use of chloroform to which some alcohol has been added.

B. F.

Occurrence of Porphyrin in Blood-serum. A. Papendieck (*Z. physiol. Chem.*, 1924, **136**, 293—306).—Contrary to the findings of Fischer and Zerweck (this vol., i, 459), and following their procedure, the author could find no positive spectroscopic evidence of the presence of porphyrin in a large number of samples taken from subjects in various conditions.

O. O.

Porphyrins from Blood-pigment. A. Papendieck (*Z. physiol. Chem.*, 1924, **134**, 158—159).—Treatment of blood, saturated with hydrogen sulphide by fuming hydrochloric acid, yields a porphyrin, isolated by neutralising the solution with sodium carbonate, and acidifying with acetic acid, which precipitates the porphyrin. Treatment of the porphyrin with 1% methyl-alcoholic hydrochloric acid results in the formation of a *methyl* ester, insoluble in alkali, dense, prismatic rods, from methyl alcohol, m. p. 221°.

W. O. K.

Natural Porphyrins. VI. Distribution of Porphyrins in Organs. Detection of a Porphyrin in Yeast. H. Fischer and K. Schneller (*Z. physiol. Chem.*, 1924, **135**, 253—293).—Coproporphyrin accompanies Kämmerer's porphyrin in the products resulting from the putrefaction of calf liver, heart, and flesh, of ox flesh, and of human liver, spleen, lung, heart, and uterus. In human back-muscle, after removal of blood, coproporphyrin is alone demonstrable. Kämmerer's porphyrin is detectable in blood-corpuscles washed with physiological salt solution and subjected to putrefaction, whilst coproporphyrin may also be present in traces if the serum has not been completely removed. Only one porphyrin is therefore derivable from red blood-corpuscles. The breast-muscle of the pigeon yields after putrefaction coproporphyrin, of which the origin is ascribed to degradation of the muscle pigment (myohæmoglobin) by lactic acid. Hydrolysis of fresh blood-corpuscles by hydrochloric acid, by pepsin, and by trypsin did not lead to the definite identification of the porphyrin. Coproporphyrin is present in putrefying fish flesh and in yeast, both fresh and putrefying. This evidence is regarded as lending support to the view that blood pigments are derived from leaf pigments with porphyrins occurring as intermediates. A possible parallelism between the dualism shown by the porphyrins and chlorophylls A and B is suggested. Kämmerer's porphyrin left in glacial acetic acid and ether for some months shows a band ($623\,\mu\mu$) characteristic of hæmatoporphyrin. Coproporphyrin has been isolated as the crystalline methyl ester from fæces derived from a purely vegetarian diet (cf. A., 1923, i, 1244; this vol., i, 459).

J. P.

Changes of Reaction of Sera. H. Plotz and M. Schoen (*Compt. rend.*, 1924, **178**, 1926—1928).—Exposure of normal horse-serum in open tubes caused an increase in p_H value, owing to the escape of carbon dioxide. A decrease in p_H took place when serum was stored aseptically in closed tubes; in one case the p_H changed from 7·33 to 6·89 after storage for 51 days at 37°.

E. M. C.

Glycolysis in Blood of Normal Subjects and of Diabetic Patients. E. Tolstoi (*J. Biol. Chem.*, 1924, **60**, 69—75).—The blood of eight normal subjects and of eleven diabetic patients was examined. Determinations of sugar at intervals up to 24 hours in the blood kept at 37° with aseptic precautions showed no difference in the glycolytic power of diabetic and normal blood. At room temperature, the glycolytic rates were diminished to about the same extent in both types of blood. Counts of the red and white corpuscles gave figures within normal limits and bearing no relationship to the rate of glycolysis. C. T. G.

Relation of p_H to Tungstic Acid Precipitation of Protein. A. T. Merrill (*J. Biol. Chem.*, 1924, **60**, 257—259).—In serum, the maximum precipitation of nitrogenous substances occurs on the acid side of p_H 5; in peptone solutions the zone of maximum precipitation is not reached until the acidity is greater than p_H 1.

C. R. H.

Neutral and Oxidised Sulphur in the Blood. J. Browinski (*Bull. Soc. Chim. biol.*, 1924, **6**, 352—356).—The deproteinised blood of horses and cattle was found to contain 9·5 to 12·0 mg. % of sulphur as sulphates and also a considerable quantity of unoxidised (neutral) sulphur. Ethereal sulphates were not found. Sulphates were precipitated and weighed as barium sulphate in the blood or serum previously deproteinised by means of trichloroacetic acid. Allowance was made for the amount of barium trichloroacetate precipitated. Neutral sulphur was determined by subtracting the sulphur as sulphates from the total sulphur found by fusion with sodium peroxide and subsequent precipitation with barium. The results do not agree with those of Denis (A., 1922, ii, 225), who found much less sulphur as sulphates and no neutral sulphur in blood. The analytical methods employed by Denis are criticised. C. T. G.

Effect of Inorganic Salts on the Chemical Changes in the Blood of the Dog after Obstruction of the Duodenum. R. L. HADEN and T. G. ORR (*J. Exp. Med.*, 1924, **39**, 321—330; cf. *ibid.*, 1923, **37**, 365, 377; **38**, 55).—Life is prolonged by sodium chloride; ammonium chloride produces an acidosis. Potassium, calcium, and magnesium chlorides do not prevent the usual rise of non-protein nitrogen and fall in chlorides, followed by death. The toxic process is hastened by iodides; the inhibitory effect of sodium bromide is much less than that of the chloride.

CHEMICAL ABSTRACTS.

Blood Changes and Clinical Symptoms following Oral Administration of Phosphates. H. A. SALVESEN, A. B. HASTINGS, and J. F. MCINTOSH (*J. Biol. Chem.*, 1924, **60**, 311—326).—Oral administration to dogs of small doses of phosphates over a long period produced no clinical symptoms; if alkaline phosphates were used no change in the composition of the blood was observed, whereas with acid phosphates there was an increase in the phosphate concentration of the serum. The rapid administration of large doses of phosphate, acid or alkaline, produced violent symptoms of tetany, accompanied by a rise in the phosphate and a fall in the calcium of the serum. The tetany resembled that previously observed in parathyroidectomised dogs (cf. A., 1923, i, 979) and, in this case also, could be relieved by injection of calcium chloride. It is therefore probably due to a decrease in the calcium concentration of the blood. C. R. H.

Effect of Administration of Calcium Salts on the Inorganic Composition of the Blood. H. A. SALVESEN, A. B. HASTINGS, and J. F. MCINTOSH (*J. Biol. Chem.*, 1924, **60**, 327—339).—Ingestion of calcium chloride produces an acidosis owing to the replacement of hydrogen carbonate ions by chloride ions in the blood. The intravenous injection of small quantities of calcium chloride produced no change in the acid–base equilibrium of the blood, but a rise in the phosphate concentration was observed. Although the calcium disappeared rapidly from the blood, it could not be subsequently recovered from the urine or fæces. In cases of Bright's disease, it was not found possible to restore the calcium content of the blood to normal by means of oral administration of calcium lactate. C. H. R.

Calcium Content of the Blood during Pregnancy. II. S. T. WIDDOWS (*Biochem. J.*, 1924, **18**, 555—561).—The results for abnormal pregnancies support the observation for normal pregnancies; a heavy demand of the fœtus for calcium at certain stages of its development is met by a perfectly balanced calcium metabolism. S. S. Z.

Relation between the Pancreas and the Carbohydrate Metabolism of Muscle. Effect of Extracts from the Gland on Lactic Acid Production *in vitro*. D. L. FOSTER and C. E. WOODROW (*Biochem. J.*, 1924, **18**, 562—574).—The pancreas contains a factor capable of causing marked inhibition in the lactic acid production of chopped muscle. This factor is not identical with trypsin or insulin, and is probably not antiglyoxalase. A method is described for making a stable preparation of the pancreas with all its enzymes intact, and details are given for making an extract of this preparation with 70% alcohol which contains the inhibitory factor in high concentration. S. S. Z.

Behaviour of β-Glucose in the Human Body and the Nature of the Glucose in Serum. S. J. THANNHAUSER and M. JENKE (*Münch. med. Woch.*, 1924, **71**, 196—198; from *Chem. Zentr.*, 1924, i, 1687).—Intravenous injection of β-glucose had the same effect on the blood-sugar curve and the excretion of sugar in the urine as αβ-glucose. The elimination of acetone in diabetes is not diminished to the same extent by β-glucose as by αβ-glucose. β-Glucose is probably a stage in the degradation of sugar.
G. W. R.

Type of Sugar Excreted in the Urine of Normal Persons. K. TALLERMAN (*Biochem. J.*, 1924, **18**, 583—585).—The sugar excreted in the urine of the normal subject as a result of an injection of phloridzin is not γ-glucose, but the ordinary αβ-variety. Sugar of the same nature is found in the urine of diabetics after such an injection. γ-Glucose is therefore unlikely to be present in normal blood. S. S. Z.

Physiological Testing of Insulin Preparations. H. PÉNAU and H. SIMONNET (*J. Pharm. Chim.*, 1924, **29**, 473—481; cf. *B.*, 1924, 74).—Exception is taken to certain details of the Canadian physiological unit for insulin, and a modified test is described.
W. T. K. B.

Insulin from the Cod Fish. Direct Application of Picric Acid to Islet Tissue. H. W. DUDLEY (*Biochem. J.*, 1924, **18**, 665—668).—The islet tissue of the cod contains, weight for weight, about ten times as much insulin as mammalian pancreas. The insulin can be obtained by treating the tissue directly with picric acid and then extracting the insulin-containing picrate with aqueous acetone and converting the picrate into a soluble hydrochloride as previously described by the author. The islet tissue of the cod collected from fish caught at varying intervals up to 24 hours previously yielded 13·1 rabbit units per g. of tissue. S. S. Z.

Preparation of Insulin. M. Somogyi, E. A. Doisy, and P. A. Shaffer (*J. Biol. Chem.*, 1924, **60**, 31—58; cf. *ibid.*, 1923, **55**, 31).—The activity of purified preparations of insulin from ox pancreas is associated always with a single, fairly well-characterised protein and probably is a property of this protein. "Insulin-protein" is relatively insoluble at a reaction of about p_H 5. Crude insulin contains, in addition, two other "isoelectric-proteins" which are inactive, one with optimum precipitation, in absence of salts, at p_H 7 or 8, and the other at p_H 4. In the pancreas extracts, there is also an "alcohol-protein," readily soluble in alcohol up to 80% and insoluble in higher concentrations, which is not precipitated on adjusting the reaction, but tends to interfere with the precipitation of "insulin-protein."

The solubility relationships, in presence and in absence of salts, of "insulin-protein" and the associated inactive proteins and the choice of acid for extraction, having been studied, a simplified method for the separation of active insulin has been worked out. Data are given illustrating the activity of different preparations.
C. T. G.

Chemical Reactions of Insulin. C. H. Best and J. J. R. Macleod (*Amer. J. Physiol.*, 1923, **63**, 390—391).—Insulin, when free from protein, does not respond to any of the colour reactions for the latter, or for adrenalin. It is not appreciably affected by moderate heat in solution of p_H 5—6; it may be heated on a boiling water-bath for 10 minutes, but is destroyed by actual boiling for 3 minutes. Insulin is absorbed from acid solution by kaolin, charcoal, etc.; it could not be shown to dialyse through a collodion membrane. The potency of insulin preparations is greatly reduced by passage through a Berkfeld filter. Insulin preparations do not contain proteolytic enzymes. A. A. E.

Chemistry of Amino-acid Deamination. W. R. Fearon and E. G. Montgomery (*Biochem. J.*, 1924, **18**, 576—582).—Cyanic acid is an important factor in the production of urea and in the maintenance of neutrality in the organism, since it is shown that the acid is formed during the oxidative deamination of glycine, sarcosine, and alanine and that it is an intermediate product of α-deamination of glycine. S. S. Z.

Biochemistry of Experimental Tetany. Urinary and Muscle Creatine in Guanidine and Parathyroid Tetany with and without Calcium Treatment. A. Palladin and L. Griliches (*Biochem. Z.*, 1924, **146**, 458—466).—In experimental guanidine and parathyroid tetany, muscle creatine is increased and appears in the urine, whilst the excretion of creatinine is unaffected or but slightly increased. A direct relationship between muscle creatine and urinary creatine and creatinine is inferred. The abolition of tetanic symptoms by injection of calcium salts into rabbits, previously treated with guanidine, arrests the excretion of creatine and restores muscle creatine to normal limits. The increase of the latter in tetany is not ascribed to its increased formation from guanidine (cf. Paton, *Quart. J. Expt. Physiol.*, 1916, **10**), since if calcium be administered simultaneously with guanidine the muscle creatine is not increased. J. P.

Sulphur Metabolism of the Dog. II. Constancy of the Relative Output of Ethereal Sulphate and of Neutral Sulphur after Oral Administration of Halogen-substituted Benzenes. T. S. Hele (*Biochem. J.*, 1924, **18**, 586—612).—Chlorobenzene administered by the mouth has an approximately constant quantitative effect on the sulphur metabolism of the dog. The "extra" ethereal sulphate bears a constant proportion to the "extra" neutral sulphur (about 2 to 3). This ratio may be altered by repeated doses of chlorobenzene if no cystine or sodium sulphate is given at the same time. The simultaneous oral administration of these latter compounds alone does not alter the ratio. The ratio of "extra" free phenol to "extra" total phenol also appears to be constant. There is no increase of free or conjugated phenols in the fæces after administration of chlorobenzene. The action of bromobenzene is similar to that of chlorobenzene: The oral administration of cystine always produces a small rise in the output of neutral sulphur. A rise in the protein intake may produce a considerable rise in the output of neutral sulphur. Guaiacol seems to have a slight toxic effect on sulphur metabolism. S. S. Z.

(Biological) Action of Sulphur. A. Hottinger (*Schweiz. med. Woch.*, 1923, **53**, 429—432; from *Chem. Zentr.*, 1924, i, 1826—1827).—A theoretical discussion of the rôle of sulphur and sulphides in biological oxidations and reductions. G. W. R.

Formation of Ethereal Sulphates. G. J. Shiple, J. A. Muldoon, and C. P. Sherwin (*J. Biol. Chem.*, 1924, **60**, 59—67).—The feeding of bromobenzene, phenol, or *p*-chlorophenol to a pig maintained on a carbohydrate diet in a condition of endogenous nitrogen catabolism definitely increased the output of ethereal sulphates in the urine. Sodium sulphate, fed with the aromatic poisons, did not cause any further increase in ethereal sulphates; with phenol and bromobenzene there was actually a decrease. Cystine, given with phenol, caused an increase beyond that obtained with phenol alone, whilst cystine with bromobenzene or *p*-chlorophenol caused a marked decrease. Ethereal sulphates are therefore not formed simply at the expense of inorganic sulphates: the sulphur required must come from the tissues, presumably from tissue-cystine, although if cystine be present in the diet, it may be utilised. It is thought that when ethereal sulphates are formed from endogenous sulphur, the phenolic poison is first linked to an intermediary product of the metabolism of tissue-cystine and the whole eventually oxidised to the sulphate stage. If exogenous cystine is available, a complex analogous to *p*-bromophenylmercapturic acid may be formed and either excreted as such or oxidised to a sulphate. C. T. G.

Influence of Salts on Metabolism. II. Blood-sugar and Liver Glycogen. M. Händel (*Biochem. Z.*, 1924, **146**, 438—445).—Withholding of cell salts from the dietary of rats produces a slight diminution in liver glycogen and a slight increase in blood-sugar. The addition of potassium has no appreciable effect, whilst calcium produces a slight increase in blood-sugar, but has no influence on the liver glycogen. The latter is likewise not affected by the addition of phosphates, which, however, produce a normal blood-sugar value. J. P.

Influence of Variations in the Sodium–Potassium Ratio on the Nitrogen and Mineral Metabolism of the Growing Pig. M. B. Richards, W. Godden, and A. D. Husband (*Biochem. J.*, 1924, **18**, 651—660).—The addition of sodium chloride or sodium citrate to a ration of cereal grain fed to a growing pig leads to increased assimilation and retention of nitrogen, calcium, and phosphorus. The increase of sodium salts in the ration causes increased excretion of potassium in the urine, which is, however, counterbalanced by the diminution of this element in fæcal excretion, and the balance is therefore normal. S. S. Z.

Mechanism of Acidosis in Anæsthesia. R. L. Stehle and W. Bourne (*J. Biol. Chem.*, 1924, **60**, 17—29).—A study of the relation between ether anæsthesia and increased excretion of phosphoric acid. C. T. G.

Classification and Grouping of Vitamins. W. Tönnis (*Z. physiol. Chem.*, 1924, **136**, 89—104).—In mice and rats, normal growth and duration of life are observed only when the diet comprises sources of all three vitamins, *A*, *B*, and *C*. The simultaneous administration to avitaminosed animals of two vitamins has a definite improving effect on the growth curve—*A* and *B* exerting a more marked effect than *A* and *C*—only during the early stages of avitaminosis. Alcoholic and weakly acidic extracts of yeast produce in adult rats, in addition to the curative effect on the paresis due to lack of vitamin-*B*, an increase in body-weight, an effect which is also shown by the extracted yeast. The presence of the supposed vitamin-*D* in yeast is therefore not confirmed. Alcoholic and aqueous yeast extracts exert no effects on the growth of young rats and mice which are not also shown by the extracted yeast itself, from which it is concluded that no evidence is forthcoming in support of the possible separation of the water-soluble growth vitamin from the anti-beri-beri vitamin, and the general conclusion is drawn that only the three vitamins, *A*, *B*, and *C*, exist. J. P.

Association of Manganese with Vitamins. J. S. McHargue (*J. Agric. Res.*, 1924, **27**, 417—424).—Manganese has been shown (cf. A., 1922, i, 906) to be an essential element in plant economy. In the animal body it is found most abundantly in the liver, kidney, and pancreas. The pericarp and germ of rice, barley, and wheat contain considerable amounts of manganese, which is largely removed during the polishing and milling processes. Cod-liver tissue, fish roe, the yolks of eggs, tomatoes, oranges, and lemons are relatively rich in manganese, whilst purified cod-liver oil and the whites of eggs contain negligible amounts. Colostrum is much richer in manganese than milk. The fact that it is found in largest quantities in those plant- and animal-tissues which show the greatest vitamin potency suggests the existence of a relationship between manganese and these vital factors. E. M. C.

Preparation of a Crystalline Picrate having the Antineuritic Properties of Vitamin-*B*. A. SEIDELL (*U.S. Public Health Rep.*, 1924, 294—299; cf. Bertrand and Seidell, *Bull. Soc. Chim. biol.*, 1923, **5**, 794).—The mixture of picrates, previously described as resulting from the treatment of an aqueous-alcoholic extract of yeast with methyl-alcoholic picric acid, can be separated to some extent by repeated extraction with acetone. From the acetone-soluble portion there was obtained a picrate crystallising in reddish-yellow flakes, m. p. (decomp.) below 160°. A daily dose of 2 mg. of this picrate is sufficient to protect pigeons against loss of weight on a diet of polished rice. The residue from the acetone extraction crystallises in pale yellow rods and prisms, m. p. 202°, and is physiologically inert. Both picrates, on combustion, give figures corresponding with the formula $C_6H_{18}O_2N_3,C_6H_2(OH)(NO_2)_3$. C. R. H.

Antiscorbutic Fraction of Lemon Juice. II. S. S. ZILVA (*Biochem. J.*, 1924, **18**, 632—637).—When decitrated lemon juice is fermented in order to remove the sugar an active solution is obtained. On concentrating such a solution and precipitating with absolute alcohol, further non-active matter is removed in the precipitate. When such purified solution is treated with basic lead acetate, the entire antiscorbutic vitamin is precipitated. On removing the lead and bringing the solution up to its original volume, a preparation is obtained which contains the entire antiscorbutic activity of the original lemon juice, but only 0·03—0·07% of solids. Basic lead acetate also brings down the vitamin entirely in unfermented decitrated lemon juice, but in this case more extraneous matter (sugar, etc.) is also precipitated with it. These active preparations reduce ammoniacal silver nitrate in the cold and decolorise potassium permanganate. A new method for the removal of acids and other non-active matter from lemon juice without vitiating its antiscorbutic activity is described. S. S. Z.

Reducing Properties of Antiscorbutic Preparations. S. J. B. CONNELL and S. S. ZILVA (*Biochem. J.*, 1924, **18**, 638—640).—The destruction of the reducing properties of antiscorbutic solutions observed by Zilva (see preceding abstract) by heat and by alkalinity in the presence of air does not proceed at the same rate as the inactivation of the vitamin by the same means. Further evidence is produced which shows that the modified Folin's reagent suggested by Bezssonnoff (this vol., i, 686, 789) for the detection of the antiscorbutic factor is untrustworthy. S. S. Z.

Differential Dialysis of the Antiscorbutic Factor. II. S. J. B. CONNELL and S. S. ZILVA (*Biochem. J.*, 1924, **18**, 641—646).—The diffusion of the antiscorbutic factor proceeds differently from that of the sugar and the nitrogenous substances present in decitrated lemon juice. The antiscorbutic factor in swede juice and in lemon juice diffuses through membranes of the same permeability. There are indications that the size of the active molecule cannot be far removed from that of the hexoses. S. S. Z.

Antiscorbutic Value of Fresh and Canned English Tomatoes. E. M. Delf (*Biochem. J.*, 1924, **18**, 674—678).—Raw fresh juice of English tomatoes is not quite as effective an antiscorbutic as fresh orange- or lemon-juice. Bottled tomatoes stored for six months were found to have lost about two-thirds of their original activity. Canning causes a loss of nearly three-quarters of the original value. A further but smaller loss takes place after storage for about 4 years. Canned tomato purée retains only about one-seventh of its original activity. S. S. Z.

Creatine Content of Brain. V. J. Harding and B. A. Eagles (*J. Biol. Chem.*, 1924, **60**, 301—310).—The percentage of creatine in the brain as a whole is a constant for any individual species; it is always higher in the cerebellum than in the cerebral hemispheres; it is independent of the amount of creatine in the diet, and it is rapidly reduced by autolysis of the brain-tissue. C. R. H.

Isolation of Arachidonic Acid from Brain-tissue. L. G. Wesson (*J. Biol. Chem.*, 1924, **60**, 183—187).—Bromine is added in slight excess to the ether extract of ground brain-tissue previously dehydrated with acetone. The white precipitate is removed, digested at 37° for 24 hours with 50% alcohol containing 5% of hydrochloric acid, washed, and dried at 100°. Analysis shows this substance to be the octabromide of arachidonic acid. The yield is about 3·5 g. per kg. of wet brain-tissue. The compound may be debrominated by boiling an alcohol solution for about 4 hours with copper-coated zinc (if the ethyl ester is required, dry hydrogen chloride is passed slowly through the boiling alcohol solution for 1 hour); water is then added and the acid (or ester) extracted with ether. The free acid thus obtained has all the properties of arachidonic acid, and there is little reason to suspect that it is different from the acid present as glyceride in the tissues. C. T. G.

Gelatinolytic Liver Enzyme. Tsou-Hia Hsü (*Biochem. Z.*, 1924, **146**, 540—544).—The gelatin-liquefying enzyme present in liver extracts (Hata, A., 1909, ii, 416) may be precipitated from fresh preparations, but not from old extracts, by ammonium sulphate. Various attempts to isolate the enzyme by precipitation with uranyl acetate, and by separation of the accompanying proteins by means of cholesterol, are described. J. P.

Hippuric Acid Balance in Renal Diseases. J. Snapper and A. Grünbaum (*Klin. Woch.*, 1924, **3**, 101—104; from *Chem. Zentr.*, 1924, i, 1689).—After administration of 3—5 g. of sodium hippurate to healthy men, only traces of hippuric acid were found in the blood, whilst in certain renal diseases 4—40 mg. % were found. Both diseased and healthy kidneys produced hippuric acid, but in the former case it was eliminated with difficulty.

G. W. R.

Extractives of Ox Spleen. J. HAGIHARA (*Z. physiol. Chem.*, 1924, **136**, 232—234).—A hot-water extract of ox spleen, after removal of the protein, gave no crystallisable substances in the arginine, histidine, and lysine fractions. O. O.

Nuclein Substance of the Spleen. J. HAGIHARA (*Z. physiol. Chem.*, 1924, **135**, 294—316).—Extracts of dried ox spleen with 10% sodium chloride, yielded, on treatment with copper sulphate or calcium chloride, precipitates with a phosphorus: nitrogen ratio of 1 : 1·5 to 1 : 2·5. On hydrolysis with 5% sulphuric acid and precipitation with ammoniacal silver nitrate, the presence of purine bases could not be established with certainty, the supposed guanine fraction giving nitrogen values which were too low. Guanylnucleic acid was not detected in the original dried gland. Various other methods of precipitating nucleic acids were applied to the preparations of the spleen, but the material obtained showed a variable composition and no very definite conclusions are drawn. J. P.

Significance of Ions in Muscular Function. G. EMBDEN and E. LEHNARTZ (*Z. physiol. Chem.*, 1924, **134**, 243—275).—A comparison was made of the effects of the sodium salts of various acids on the breakdown of lactacidogen in freshly-chopped muscle, to give lactic and phosphoric acids. In this respect, the ions arrange themselves according to the Hofmeister series, the greatest effect being obtained with thiocyanate and iodide and scarcely any with sulphate and tartrate. Sodium citrate and, especially, sodium fluoride, bring about the reverse reaction, viz., a disappearance of inorganic phosphate and synthesis of lactacidogen. The power of the different ions to stimulate breakdown of lactacidogen is found to correspond with their power to restore activity to a frog's muscle which has been inhibited by keeping in sucrose solution or otherwise.

C. R. H.

Significance of Ions in Muscle Functions. II. Influence of Sodium Fluoride Solutions on Lactic Acid Formation in Frog-muscle Pulp. G. EMBDEN, A. ABRAHAM, and H. LANGE (*Z. physiol. Chem.*, 1924, **136**, 308—312).—Sodium fluoride in concentrations of $M/100$, $M/10$, and $M/1$ favoured the formation of lactacidogen but inhibited the lactic acid formation almost completely. At low concentrations ($M/1000$—$M/10{,}000$), the formation of lactacidogen is diminished and lactic acid formation increased. When the sodium fluoride solutions contained 2% of sodium hydrogen carbonate similar relations held, but the extent to which lactacidogen synthesis or lactic acid formation occurred was usually greater.

O. O.

Hydrolysis of Protein by a Heat-stable Catalyst Present in Muscle. W. M. Clifford (*Biochem. J.*, 1924, **18**, 669—673).—Cod muscle contains a heat-stable catalyst which hydrolyses protein. S. S. Z.

Possible Significance of Hexosephosphoric Esters in Ossification. II. The Phosphoric Esterase of Ossifying Cartilage. R. Robison and K. M. Soames (*Biochem. J.*, 1924, **18**, 740—754).—The phosphoric esterase described by Robison which is present in bone and ossifying cartilage is also present in equally high degree in teeth, especially in those of very young animals. This enzyme also hydrolyses ethyl butyrate and triacetin, but not olive oil. It is distinct from the esterase of pancreas, which is relatively inactive towards phosphoric esters. The optimum reaction of the enzyme is p_H 8·4—9·4—a reaction favourable for the precipitation of tertiary calcium phosphate and calcium carbonate. The deposition of fresh calcium phosphate has been demonstrated in bones taken from rachitic rats in solutions of calcium hexosemonophosphate or calcium glycerophosphate at 37° at the above reaction. It is argued that the enzyme is secreted in the region of the osteoblasts and hypertrophic cartilage cells and is actively concerned in ossification. It is suggested that the reaction of the tissue fluid in the region of ossification is rendered more alkaline than the blood by some mechanism, thereby increasing the activity of the enzyme, and favouring the deposition of both calcium phosphate and carbonate. S. S. Z.

Possible Significance of Hexosephosphoric Esters in Ossification. III. Action of the Bone Enzyme on the Organic Phosphorus Compounds in Blood. H. D. Kay and R. Robison (*Biochem J.*, 1924, **18**, 755—764).—The acid-soluble organic phosphorus compounds present in the blood of various animals consist of at least two phosphoric esters, one of which is rapidly hydrolysed by the enzyme of ossifying cartilage (see preceding abstract), whilst the other is very resistant to the action of this enzyme. Both esters are hydrolysed by boiling with 0·2*N*-sulphuric acid. A method has been worked out by which the respective amounts of these esters may be determined and results of such determinations are given for the blood of human adults and children, and of rats, rabbits, and cockerels. The amount of ester hydrolysed by the bone enzyme varies between 14 and 36% of the total acid-soluble phosphorus. This ester is present almost entirely in the corpuscles. Attempts to demonstrate the presence of hydrolysable esters in the plasma lead to inconclusive results. There are indications that the esters are able to diffuse from the corpuscles to the plasma. The phospholipins present in the blood are not hydrolysed by the bone enzyme. S. S. Z.

Cholesteryl Palmitate, a Constituent of Corpus Luteum. M. C. Hart and F. W. Heyl (*J. Amer. Pharm. Assoc.*, 1924, **13**, 17—22).—Dried corpus luteum contained 4·5—5·4% of ash.

Cholesteryl palmitate, potassium stearate, free fatty acids, and possibly cholesteryl stearate were identified in the acetone extract.
CHEMICAL ABSTRACTS.

Microchemical Detection of a Nucleic Acid of the Thymonucleic Acid Type and the Selective Coloration Dependent Thereon in Microscopic Preparations. R. FEULGEN and H. ROSSENBECK (*Z. physiol. Chem.*, 1924, **135**, 203—248).—A colour test called the " nucleal reaction " is described, whereby the presence of nucleic acids of the type of thymonucleic acid may be demonstrated in micro-preparations by the development of a red colour after these have been submitted to mild hydrolysis (4 minutes at 60° with $0{\cdot}1N$-hydrochloric acid), followed by treatment with fuchsin–sulphurous acid. The reaction is given by nucleic acids containing a hexose residue, such as thymus-nucleic acid, but not by the nucleic acids containing a pentose such as yeast-nucleic acid and triticonucleic acid. Nevertheless, certain of the higher plants (wheat embryos, bulbous plants) give a positive reaction, and it is inferred that in these cases a hexose acid must be present in addition to the well-established pentose acid. This is paralleled by the occurrence in animal cells of such pentose nucleotides as inosinic and guanylic acids. The nuclei of ciliate protozoa (infusoria) give the nucleal coloration, but in still lower representatives of the class (trypanosomes) it is absent. Bacteria are also, like yeast-cells, " anucleal." Yeast-nucleic acid, typical of the lower plants, is regarded as being the primitive form of the substance; it becomes partly replaced in the higher plants by the " nucleal " acid, and the primitive form almost entirely disappears in the animal world, surviving only in the form of the pentose nucleotides. The nucleic material occurring in rye and responsible for the nucleal reaction *in the higher plants has been isolated in an impure condition.* It is rich in phosphorus and gives a marked reaction with fuchsin–sulphurous acid after mild hydrolysis just as does thymus-nucleic acid.
J. P.

Mechanism of "Nucleal" Staining. I. Detection of Reducing Groups in the Nuclei of Partly Hydrolysed Micro-preparations. R. FEULGEN and K. VOIT (*Z. physiol. Chem.*, 1924, **135**, 249—252).—The nuclei of partly hydrolysed preparations of frog erythrocytes give a brown coloration, due to reduced colloidal silver when treated with a saturated aqueous solution of silver oxide. The reaction is not given by non-hydrolysed preparations. The presence of reducing groups liberated by hydrolysis of the nuclear material is inferred.
J. P.

Mechanism of "Nucleal" Staining. II. Behaviour of the Nucleus of Partly Hydrolysed Microscopic Preparations to Magenta–Sulphurous Acid after Preliminary Treatment with Phenylhydrazine. R. FEULGEN and K. VOIT (*Z. physiol. Chem.*, 1924, **136**, 57—61).—The " nucleal " colour reaction (cf. preceding abstracts) is given by partly hydrolysed (4 mins. at 60° in $1{\cdot}0N$-hydrochloric acid) micro-preparations, but not after these have been treated with phenylhydrazine acetate. Preparations treated with acid for 1 min., then with phenylhydrazine, and subsequently hydrolysed further, give the reaction, which is therefore ascribed to a chemical combination between magenta-sulphurous acid and the aldehyde groups liberated by separation of the purine residues of the nucleic acids during mild hydrolysis. J. P.

Iron Content of Nucleoproteins. T. Takahata (*Z. physiol. Chem.*, 1924, **136**, 214—218).—The rôle of iron which occurs in the precipitate of nucleoproteins obtained with acetic acid from an aqueous extract of an organ is not quite clear. In analogy with the iron of the blood pigments, it may have some significance in oxidation processes or it may have a direct relation with the red blood-corpuscles and their genesis. It appears very doubtful whether the iron of the nucleoproteins can participate at all in oxidation processes. As nucleic acids are known to be free from iron and most proteins contain it only in traces, the iron content of different nucleoproteins has been examined. It is found that most extracts of different organs contain a sufficient amount of inorganic iron salts, a certain amount of which is precipitated with the nucleoprotein.
D. R. N.

Production of Ammonia and Urea in Autolysis. R. A. McCance (*Biochem. J.*, 1924, **18**, 486—497).—The optimum hydrogen-ion concentration for the production of ammonia and urea by autolysis from spleen and kidney is p_H 6. When liver is employed in the winter the optimum p_H for ammonia production is the same but it is not so marked. The optimum for urea production lies in the region of p_H 5—5·5. During the summer, the ammonium curves are unchanged, but the production of urea at p_H 5—5·5 falls to a value often lower than that at p_H 6. When the tissues are autolysed in the presence of oxygen and hydrogen, the total nitrogen is always the same, and also the p_H. The ammonia is sometimes the same and sometimes slightly higher in the hydrogen filtrate. The urea is always very much greater in the hydrogen filtrate, and the amount of urea produced in an autolysis in hydrogen is the same as when the gas is not present during the process. Nitrogen and hydrogen give identical results. The production of ammonia is common to all autolyses; that of urea occurs only in certain organs. It is not produced in the case of mammalian pancreas (bullock, pig), lung, skeletal muscle (bullock), heart-muscle (sheep) or avian liver (hen). Ammonia and urea are formed by separate processes. Their precursors are discussed. An enzyme which forms part of the urea-producing system and is strongly inhibited by gaseous oxygen is described and discussed. S. S. Z.

Occurrence of Agmatine in Lower Animals. F. Holtz (*Z. Biol.*, 1924, **81**, 65—67).—An extract of the giant siliceous sponge, *Geodia gigas*, was found to contain agmatine, a base already known to occur in vertebrates and in some lower plants, but not hitherto found in any invertebrate. The substance was isolated as the picrate from the arginine fraction of the extract. It was identified by the composition and properties of the picrate, chloroaurate, and carbonate. Arginine was not found in the extract of *G. gigas*.

C. T. G.

Occurrence of Trigonelline in the Animal World. F. HOLTZ, F. KUTSCHER, and F. THIELMANN (*Z. Biol.*, 1924, **81**, 57—60).—Trigonelline, hitherto found only in plants, is now reported as occurring in the sea-urchin *Arbatia pustulosa.* The extract of 109·5 kg. of the animals was treated according to Kutscher's method (*Z. Nahr. Genussm.*, 1905, **10**, 528; A., 1906, ii, 562) and 13 g. of the gold salt of the alkaloid were isolated from the "lysine fraction." The alkaloid was identified by analyses and m. p. of the chloroaurate, chloroplatinate, chloride, and of the free base. Roeder's observation (A., 1914, i, 25) that the potassium ferrocyanide compound of trigonelline crystallises as red, lustrous prisms (the corresponding compound of glycine-betaine being white) was confirmed with trigonelline prepared from nicotinic acid and from sea-urchins.

The discovery of trigonelline in the animal world makes the occurrence of methylpyridinium hydroxide in crabs, sea-anemones, and other animals more easily intelligible, since this compound may be formed from trigonelline by addition of water and loss of carbon dioxide. C. T. G.

Recognition of Arginine, Betaine, Choline, and Acanthine in the Embryos and Liver of the Spiny Dog-fish (*Acanthias vulgaris*). E. BERLIN and F. KUTSCHER (*Z. Biol.*, 1924, **81**, 87—92).—The presence in various cold-blooded animals of certain "intermediate" products of metabolism such as betaines and methylpyridinium hydroxide, which normally occur in plants, has recently been demonstrated. From the aqueous extract of about 1 kg. of the embryos of the common dog-fish (*Acanthias vulgaris*), arginine, betaine (12 g.), and choline (0·5 g.) were isolated from the phosphotungstic precipitate, whilst from the filtrate from the latter was isolated about 1 g. of a substance, $C_{15}H_{22}O_4N_4$, m. p. 122—124°, for which the name *acanthine* is suggested. It does not give the biuret or tryptophan reactions, but gives Pauly's diazo-reaction.

Betaine and choline were also found in the liver of the dog-fish. The embryos contain 1·2% of betaine and the liver and muscle about 0·07%; similarly, young beetroots contain more betaine than the older plants, indicating that in both plants and animals the substance is formed in the early stages and utilised during growth.

C. T. G.

Changes in Chemical Composition of the Tissues of the Herring in Relation to Age and Maturity. J. R. BRUCE (*Biochem. J.*, 1924, **18**, 469—475).—At any given stage of sexual maturity, the water, fat, and protein contents of the fresh muscle substance of the herring are dependent on age, the older fish containing a lower percentage of water and protein and a higher percentage of fat. This variation in composition with age resembles that previously observed to be associated with the successive stages of sexual maturation. The metabolic demands of the growing gonads are made first on the fatty reserves of the liver. The muscular tissue is depleted only shortly before spawning. There are indications that the developing gonads have a high phosphorus requirement and that phosphatides play a part in the tissue changes and translocation associated with maturation. S. S. Z.

Culture of the Marine Diatom *Nitzschia closterium* (F.) *minutissima* in Artificial Sea-water. E. A. Peach and J. C. Drummond (*Biochem. J.*, 1924, **18**, 464—468).—This organism can grow and thrive in an inorganic culture medium, and does not require an organic substance specific to its growth. S. S. Z.

Occurrence of Lactase in the Alimentary Tract of the Chicken. T. S. Hamilton and H. H. Mitchell (*J. Agric. Res.*, 1924, **27**, 605—608; cf. following abstract, and Plimmer and Rosedale, A., 1922, i, 485).—Lactase is present in the crop, but absent from the proventriculus, the pancreas, and the intestines of normal chickens. E. M. C.

Utilisation of Lactose by the Chicken. T. S. Hamilton and L. E. Card (*J. Agric. Res.*, 1924, **27**, 597—604).—The lactose present in the whole or skim milk, whey, or buttermilk consumed by chickens will be completely absorbed. Lactose was utilised fairly completely in amounts up to 8 g. per hen per day, although such amounts invariably produced acute diarrhœa. Large amounts of uric acid interfere with the Munson-Walker-Bertrand method, but not with the Benedict method, for the determination of reducing sugars. E. M. C.

Reducing and Oxidising Reaction in Milk. P. Haas and B. Lee (*Biochem. J.*, 1924, **18**, 614—620).—Itate and peroxydase are not identical, since they can be partly separated. Itate does not oxidise nitrite directly. It forms a peroxide by acting on the acetaldehyde present, which in its turn is utilised by the peroxydase of the milk in oxidising the nitrite. Attempts to effect a similar oxidation of nitrite by a peroxydase of vegetable origin in the presence of hydrogen peroxide have so far been unsuccessful. S. S. Z.

Fission and Synthesis of Esters by Lipase from the Lacteal Glands and from Milk. A. I. Virtanen (*Z. physiol. Chem.*, 1924, **137**, 1—13).—An investigation of the fission and synthesis of esters by the expressed juice and the glycerol extract of the lacteal glands of cattle. The lipolytic properties of these glands are very feeble. In the quantitative experiments only the glycerol extract was used, and concordant results were obtained only when p_H was maintained constant throughout. Under these conditions the hydrolysis of ethyl butyrate at 40° follow the course of a unimolecular reaction. In a series of experiments in which p_H varied from about 8·7 to about 5, the velocity of hydrolysis decreased with decrease in p_H, finally ceasing at a value somewhat below 5. This cessation was not due to the destruction of the lipase by the acidity of the solution. Attempts to esterify butyric acid with glycerol failed, but the synthesis of ethyl butyrate was effected. Synthesis occurs at p_H values up to about 4, but beyond this value the reaction ceases. Whole milk acted hydrolytically at p_H 8·8. B. F.

Secretion of Bile. III. E. Neubauer (*Biochem. Z.*, 1924, **146**, 480—485).—In continuation of previous work (*ibid.*, 1922, **130**, 556), it is shown that dehydrodeoxycholic acid is a powerful cholagogue, somewhat more active than deoxycholic acid, whilst in its hæmolytic action it is somewhat weaker than both deoxycholic and cholic acids. In 1·5% aqueous solution sodium dehydrodeoxycholate has a surface tension higher than that of sodium deoxycholate and cholate, and lower than that of sodium dehydrocholate. Dehydrodeoxycholic acid is less toxic in its cardiac effects than deoxycholic acid. It is concluded that hæmolytic and toxic action in the bile acid group increases with surface activity, whilst the latter is not related to cholagogic properties. J. P.

Blood and Spinal Fluid. II. Calcium, Magnesium, and Phosphorus. N. G. Barrio (*J. Lab. Clin. Med.*, 1923, **9**, 54—56).—The spinal fluid contains (in mg. per 100 c.c.) 4·6—6·1 of calcium, 1·5—2·7 of inorganic phosphorus, and 1·4—6·1 of magnesium. The concentrations are, respectively, 50%, 50%, and 125% of those of the blood-serum. Chemical Abstracts.

Analysis of Liquid Produced in a State of General Oedema. R. Fabre (*J. Pharm. Chim.*, 1924, **29**, 484—485).—The pale yellow, feebly acid liquid (d^{15} 1·009) contained, per litre, protein 1·2 g., urea 0·92 g., uric acid nitrogen 0·43 g., combined ammonia 0·034 g., ammoniacal nitrogen 0·028 g., total nitrogen 0·66 g., and sodium chloride 5·73 g.; ratio of uric acid nitrogen to (total—protein) nitrogen, 0·85. The blood, at the time of puncturing, contained 0·89 g. of urea per litre. W. T. K. B.

Excretion of Uric Acid in the Urine of Dogs. P. Mederhoff (*Z. physiol. Chem.*, 1924, **137**, 85—88).—After feeding on potato until the urine was free from uric acid, pure uric acid was mixed with the diet of a dog; no uric acid was excreted in the urine until the administration of the pure substance reached 2 g. per day. With larger doses, the quantity excreted increases with the dose. When meat was substituted for potato in the diet, the excretion of uric acid was somewhat greater than before; it is shown that this is not due to the purine content of meat. It is concluded that the power of dogs to decompose uric acid is quite low, and hence that the amount of purine derivatives which may be formed intermediately in the course of the metabolism of the dog is not very large. B. F.

Significance of Determinations of Uric Acid in Urine, Particularly in Gout, Related Diseases, and Uric Acid Diathesis. M. Weintraut (*Arch. Pharm.*, 1924, **262**, 48—52).—The results obtained in the determination of uric acid in the urine are mainly of significance when compared with the amount of acid phosphates present (Zerner's coefficient) and with the urea (coefficient of uric acid diathesis); their clinical significance is discussed.

G. M. B.

Fat Excretion. II. Quantitative Relations of the Fæcal Lipoids. W. M. Sperry and W. R. Bloor (*J. Biol. Chem.*, 1924, **60**, 261—287).—An exhaustive fractionation of the lipoid content of the fæces of cats and dogs under various dietary conditions showed that the total lipoid excretion is almost as great on a fat-free diet as on one rich in fats; it is less on a "sham-feeding" diet of agar and bone-ash. The relationships between the individual fractions and the total lipoid are not markedly affected by changes in the diet except that an increase in the intake of fatty acids calls forth an increase in the excretion of fatty acids of the same nature. There is, in general, a close resemblance between the lipoid material of the fæces and that found in the blood. The authors suggest that the fat excreted in the fæces does not originate directly from the fat of the food, but represents an excretion of lipoid materials from the blood.

C. R. H.

Presence of Pyruvic Acid in the Contents of the Intestine. A. Berthelot and G. Amoureux (*Bull. Soc. Chim. biol.*, 1924, **6**, 338—339).—Pyruvic acid was found in the fæces of a subject whose intestinal flora was rich in *Bacillus aminophilus* and whose food for several years had consisted solely of fruit, vegetables, starchy materials, sugar, butter, and a little milk. Before the experiment, a quantity of potatoes was taken in addition to the usual ration and, in the evening, 8 g. of precipitated chalk. Pyruvic acid was also detected in the contents of the small intestine of a guinea-pig fed for 4 days on bread and potatoes treated with a rich culture of *B. aminophilus*, but not in the large intestine, where it is no doubt utilised by bacteria, thus accounting for its absence from normal fæces.

C. T. G.

Minimal Lethal Doses of Lead Salts Intravenously Injected. L. Scremin (*Arch. expt. Path. Pharm.*, 1924, **101**, 207—217).—From experiments on the intravenous injection into rabbits of lead nitrate, chloride, iodide, sulphate, carbonate, sulphide, and phosphate (the first two in true solution, the remainder in colloidal solution), it was found that the toxicity of the salts diminished in the above order, which is also the order of diminishing solubility. The salts fall into three groups, the first consisting of the nitrate, chloride, and iodide (and acetate), all of which are very toxic. Of the remainder, all except the phosphate are in an intermediate group of moderate toxicity; the phosphate is only slightly toxic.

H. J. P.

Influence of Phosphorus Poisoning on Muscle Creatine and on Creatine–Creatinine Excretion. A. Palladin and A. Kudrjawzewa (*Z. physiol. Chem.*, 1924, **136**, 45—56).—Phosphorus-poisoned rabbits show an increase in muscle creatine and an increased creatinine excretion with associated creatinuria. This is correlated with a diminution in lactacidogen in the muscle, with a hypoglycæmia, and with a general diminution in carbohydrates.

J. P.

Viscosity and Toxicity of Arsphenamine [Salvarsan] Solutions. C. Voegtlin, J. M. Johnson, and H. Dyer (*U.S. Public Health Rep.*, 1924, 179—195).—Dilute solutions of salvarsan on keeping undergo a progressive diminution in toxicity; at the same time there is a diminution in the viscosity of the solution. Investigation of a large number of samples, both of the hydrochloride and of the di-sodium salt, showed that this relationship between viscosity and toxicity is a general one. C. R. H.

Pharmacology of Benzyl Alcohol and Esters. I. Effect of Benzyl Alcohol, Acetate, and Benzoate (per os). II. (Intravenously.) C. M. Gruber (*J. Lab. Clin. Med.*, 1923, **9**, 15—33, 92—112).—The action of benzyl acetate and benzoate is not dependent on their hydrolysis to benzyl alcohol.

Chemical Abstracts.

Hypoglycæmic Action in Bases of the Choline Group. A. Madinaveitia and S. Hernández (*Anal. Fís. Quím.*, 1924, **22**, 168—173).—The ethyl ester of betaine produces hyperglycæmia in rabbits. G. W. R.

Ethyl*iso*amylbarbituric Acid, an Anæsthetic without Influence on Blood-sugar Regulation. J. H. Page (*J. Lab. Clin. Med.*, 1923, **9**, 194—196).—Ethyl*iso*amylbarbituric acid has little or no influence on blood-sugar in amounts sufficient to produce surgical anæsthesia. Chemical Abstracts.

[Physiological Effect of Iodine Solutions.] E. Rupp.—(See ii, 562.)

Toxicity of Copper Sulphate to the Spores of *Tilletia tritici* (Bjerk.), Winter. F. N. Briggs (*Univ. Calif. Pub. in Agric. Sciences*, 1923, **4**, 407—412).—The germination of spores of *Tilletia tritici* was inhibited by 0·002*N*-copper sulphate but was not affected by solutions more dilute than 0·0004*N*. E. M. C.

Organic Mercury Compound with Powerful Germicidal Properties. G. W. Raiziss and M. Severac (*J. Lab. Clin. Med.*, 1923, **9**, 71—80).—4-Nitro-3 : 5-diacetoxydimercuri-*o*-cresol is a powerful germicide and has a high mercuric chloride index; it is a non-irritant and has low toxicity when given intramuscularly. It does not precipitate proteins in 1 : 200 concentration.

Chemical Abstracts.

Antiseptic Action of Compounds of the *apo*Cyanine, Carbocyanine, and *iso*Cyanine Series. C. H. Browning, J. B. Cohen, S. Ellingworth, and R. Gulbransen (*Proc. Roy. Soc.*, 1924, **B**, **96**, 317—333).—In general, the compounds tested had a more powerful antiseptic effect on *Staphylococcus aureus* than on *Bacillus coli*, and there appears to be no relation between the chemical nature of the substances and their antiseptic effect. In the *apo*cyanine and *iso*cyanine series, the introduction of amino groups tends to diminish rather than to enhance the antiseptic effect. The addition of side-chains to the quinoline fraction of the molecule in the *iso*cyanine series, in contrast to their presence in the 2-methylquinoline fraction, reduces the antiseptic effect. O. O.

Antiseptic Action of Benzoic Acid, Salicylic Acid, Cinnamic Acid, and their Salts. H. I. WATERMAN and P. KUIPER (*Rec. trav. chim.*, 1924, **43**, 323—325).—The growth of *Penicillium glaucum* in liquid media at room temperature was greatly hindered by 0·05—0·1% of benzoic acid (p_H 4·4—4·0), 0·05—0·06% of cinnamic acid (p_H 4·8—4·4) or 0·04—0·06% of salicylic acid (p_H 4·8—3·4). Much larger concentrations of the sodium salts (p_H 6·5—6·4) were without much influence. The inhibiting action is not due to hydrogen-ion concentration, but is explained by the Meyer-Overton lipoid theory, which attributes antiseptic action to undissociated molecules of the organic acid (cf. Vermast, A., 1922, i, 406). The checking of growth by borax at a concentration (on anhydrous salt) of 0·2—0·3% (p_H 8·2—8·4) is, however, undoubtedly due to hydroxyl ions, since it occurred at the same p_H with sodium hydroxide or carbonate. E. H. R.

Influence of Hydrogen-ion Concentration in the Presence of Salts on the Growth of *Gibberella Saubinetii*. H. LUNDEGÅRDH (*Biochem. Z.*, 1924, **146**, 564—572).—The growth of cultures of *Gibberella*, which is increased at a given hydrogen-ion concentration by the presence of salts, shows a maximum at p_H 6·8 in the presence of phosphate, whilst in the presence of calcium the maximum occurs at p_H 4·7. An antagonism between hydrogen- and calcium-ion concentrations is inferred. Calcium diminishes the inhibiting action of magnesium on the fungus. Ammonium salts give a reaction similar to that of calcium but less well marked, whilst aluminium is very toxic. J. P.

Synthesis of Starch from Sugar by Bacteria. E. C. GREY (*Biochem. J.*, 1924, **18**, 712—715).—Bacteria synthesise starch abundantly from dextrose. This formation of the polysaccharide can only be observed at a very early stage of the fermentation; the synthetic period in this investigation was found to be over in about 40 hours. S. S. Z.

Oxygen Uptake of Bacteria. A. B. CALLOW (*Biochem. J.*, 1924, **18**, 507—518).—The oxygen uptake of spore-forming and non-spore-forming aërobic bacilli, spore-forming anaërobic bacilli, and aërobic cocci was studied. The organisms were washed free from culture medium, emulsified in sterile buffer solution, p_H 7·6, and investigated for the oxygen uptake at 22° in Barcroft's micro-respirometer. Hydrogen-ion concentration had no appreciable effect on the oxygen uptake. Bacteria grown on agar or dextrose tryptic broth gave the same oxygen uptake as when grown on tryptic broth. *Bacillus pyocyaneus*, *B. fluorescens*, *B. prodigiosus*, *B. alcaligenes*, *B. proteus*, *B. coli*, Timothy grass bacillus, *B. megatherium*, *B. subtilis*, *Staphylococcus aureus*, and *Sarcina aurantiaca*, took up large amounts of oxygen (5—25 c.c. per hour per g. of dry weight) at a steady rate. *B. alcaligenes*, *S. aureus*, and Timothy grass bacillus took up nearly as much oxygen when dried in a vacuum and emulsified in a buffer solution as before drying. *B. pyocyaneus*, on the other hand, took up oxygen after being dried at a much reduced rate. The aërobe *S. acidi lactici*, like the anaërobe *B. sporogenes*, took up only a minute amount of oxygen, at a rapidly decreasing rate. The presence of catalase did not alter the oxygen uptake of *S. acidi lactici* or *B. sporogenes*. S. S. Z.

Equilibria between Succinic, Fumaric, and Malic Acids in the Presence of Resting Bacteria. J. H. Quastel and M. D. Whetham (*Biochem. J.*, 1924, **18**, 519—534).—Resting cells (*i.e.*, a saline emulsion of the organism grown for 2 days) of *Bacillus coli* and *B. pyocyaneus*, possess an enzyme, similar to that present in muscle, which is capable of bringing about a reduction of methylene-blue in presence of sodium succinate with the formation of fumaric acid. This reaction is reversible. The effect of varying p_H on the times of reduction is a summation of the effect on the physical structure of the organism and the effect on the chemical reaction. Below p_H 5·0 no apparent reduction can be obtained and the organism appears to be coagulated. The velocity of reduction increases rapidly with increase of p_H from 6·0 to 9·0 but not above this figure. The effect of heat on the reaction at constant p_H is also a summation of two superimposed effects as mentioned above. The reduction velocity increases with increase of temperature. The temperature coefficient between 30° and 60° is 2·1. The temperature of 45° is very suitable for a high velocity of reduction without risk of injury to the organism. The rate of reduction is roughly directly proportional to the concentration and the organism present. The rate of decolorisation of the methylene-blue and the equilibrium constant of this equation are also worked out. The reversible equilibrium fumaric acid $\rightleftharpoons$ *l*-malic acid exists in presence of resting organism, fumaric acid in small quantities having been isolated after the action of the resting organism on *l*-malic acid. It has been shown that fumaric acid readily absorbs oxygen in presence of resting organisms although it will not donate hydrogen to methylene-blue.

S. S. Z.

Effect of Oxygen Supply on the Metabolism of *Bacillus coli communis*. M. Stephenson and M. D. Whetham (*Biochem. J.*, 1924, **18**, 498—506).—The carbon dioxide output and oxygen uptake of *B. coli* on a dextrose inorganic medium were studied. The organism is almost anaërobic during the early stages of dextrose breakdown. In an atmosphere of oxygen there is an increase in carbon dioxide output and a larger increase in oxygen uptake, which is not associated in the early stages of the experiment with increased utilisation of dextrose. Metabolism continues longer in oxygen than in air, the limiting hydrogen-ion concentration not being reached so soon. The increase of gaseous exchange with increase of oxygen pressure is attributed to the action on some acid degradation product of dextrose; this is supported by the observation that the disappearance of lactic acid (as the ammonium salt) with the production of carbon dioxide is greatly increased with increased oxygen tension. The growth of the organism does not take place on lactic acid under anaërobic conditions. Succinic and acetic acids and glycerol are also suitable sources of carbon for *B. coli* in air but not under anaërobic conditions. S. S. Z.

Use of Clark and Lubs Indicators for the Detection of Acid Production by the Colon–Typhoid Group. P. A. Tetrault (*Proc. Indiana Acad. Sci.*, 1922, 247—252).—Complete data are tabulated for the use of bromocresol-purple, bromothymol-blue, and phenol-red as indicators, whereby bacteria of the colon-typhoid group (*Bacillus coli, B. typhosus, B. dysenteriæ, B. paratyphosus A* and *B*, and *B. enteritidis*) can be distinguished in their formation of acid from dextrose, lactose, sucrose, maltose, raffinose, mannose, dulcitol, xylose, rhamnose, arabinose, lævulose, and galactose. The above indicators are mentioned in increasing order of sensitiveness. Chemical Abstracts.

Transformation of Carbon Compounds by *Bacillus pyocyaneus*. J. Supniewski (*Compt. rend. Soc. Biol.*, 1923, **89**, 1377—1379; from *Chem. Zentr.*, 1924, i, 1679).—Sodium acetate when added to cultures of *B. pyocyaneus* is rapidly decomposed, probably with formation of formaldehyde and formic acid. Acetaldehyde is oxidised to acetic acid. Acetone gives formic and acetic acids. Ethyl alcohol gives acetaldehyde and acetic acid. Lactic acid gives pyruvic and acetic acids, acetaldehyde, and carbonates. Glycerol is oxidised to carbon dioxide. Dextrose is rapidly attacked. Cultures containing aliphatic compounds with carboxyl groups become alkaline by oxidation of these groups, whilst compounds containing the groups $-OH$, $=CO$, or $-CHO$ become acid through oxidation to acids. The limit on the alkaline side is p_H 8·8 and on the acid side p_H 6·6. G. W. R.

Transformation of Nitrogen Compounds by *Bacillus pyocyaneus*. J. Supniewski (*Compt. rend. Soc. Biol.*, 1923, **89**, 1379—1380; from *Chem. Zentr.*, 1924, i, 1679; cf. preceding abstract).—*B. pyocyaneus* readily assimilates ammoniacal and nitrate nitrogen, the oxygen in the latter case being also utilised. Carbamide is decomposed to ammonium carbonate by means of a urease. Glycine is not readily attacked. Asparagine is first deamidised with formation of ammonium aspartate and, ultimately, ammonium malate. Cyanogen compounds are assimilated after being converted into ammonium compounds. G. W. R.

Metabolism of Cyclic Compounds by *Bacillus pyocyaneus*. J. Supniewski (*Biochem. Z.*, 1924, **146**, 522—535).—*B. pyocyaneus* is unable to utilise most benzene derivatives, nor are aminobenzenes suitable as sources of nitrogen. Salicin is decomposed, the dextrose residue being utilised and the saligenin oxidised to salicylic acid. Aliphatic and cyclic amino-acids are decomposed with destruction of the carboxyl group and liberation of ammonia. Tryptophan is decomposed with, apparently, the intermediate formation of anthranilic acid. The bacillus acts very slowly on indole itself. Anthranilic acid is decomposed to form ammonium carbonate whilst *p*- and *m*-aminobenzoic acids are not attacked. These two last-mentioned acids together with *o*- and *m*-aminocinnamic acids do not serve as sources of carbon or nitrogen. J. P.

Oxidation and Reduction by *Pneumococcus*. I. Production of Peroxide by Anaërobic Cultures of *Pneumococcus* on Exposure to Air under Conditions not Permitting Active Growth. II. Production of Peroxide by Sterile Extracts of *Pneumococcus*. O. T. Avery and J. M. Neill (*J. Exp. Med.*, 1924, **39**, 347—355, 357—366).—I. When grown anaërobically, pneumococci form peroxide on exposure to molecular oxygen with a rapidity which varies with the condition of the culture; the effect is not dependent on active cell-growth.

II. At p_H 5—9, sterile extracts of unwashed cells form peroxide on exposure to the air. Chemical Abstracts.

Growth-inhibitory Substances in *Pneumococcus* Cultures. H. J. Morgan and O. T. Avery (*J. Exp. Med.*, 1924, **39**, 335—346).—A study of the effect of hydrogen peroxide on the growth of *Pneumococcus* and *Staphylococcus aureus*, and of the latter in filtrates from cultures of the former. Chemical Abstracts.

Chemical Evidence on the Phylogenetic Classification of the Tubercle Bacillus. E. R. Long (*Amer. Rev. Tuberculosis*, 1923, **8**, 195—213).—The fairly definite animal tendencies of the tubercle bacillus are: a nucleic acid probably identical with that of the thymus, pancreas, sperm, and spleen. The basis, therefore, lies in the established presence of the pyrimidines, thymine, and cytosine, in tubercle bacillus nucleic acid, and the presence of a hexose, and the established absence of uracil. The fairly definite plant tendencies are: a marked chemosynthetic power in nitrogen metabolism; synthesising such complex substances as amino-acids and purine bases with no source of nitrogen other than ammonia. The less definite animal tendencies are: the said possession of lipins of the diamino-monophosphatide type, which so far have been described convincingly only in animals. The less definite plant tendencies are: the said content of hemicellulose or pentosans, made up of pentose units, which are typical plant substances, and an appreciable content of lauric acid, which has a wide plant distribution. Chemical Abstracts.

Enzymic Studies on Lactic Acid Bacilli. A. I. Virtanen (*Z. physiol. Chem.*, 1924, **134**, 300—319).—Lactic acid fermentation is a unimolecular reaction. Attempts to demonstrate a synthesis of hexose phosphate from mixtures of inorganic phosphate and dextrose or lactose were entirely negative, both with the living organisms and with dried preparations. Lævulose diphosphate was not affected by lactic acid bacilli. Catalase was entirely absent from the organisms. The living bacteria, but not the dried preparations, have the power of reducing methylene-blue; it is suggested that the reducing power of milk towards methylene-blue is due partly to the presence of bacteria. C. R. H.

Production of Formaldehyde by Intestinal Bacteria. B. H. Shaw (*Brit. Med. J.*, 1924, I, 461—463).—From 0·0001 to 0·0015% of formaldehyde was produced by the action of various intestinal bacteria on peptone alone and admixed with lactose, dextrose, mannitol, or inulin. Bacteria do not appear to be capable of producing formaldehyde when oxygen is excluded. A. A. E.

Influence of Sodium Pyruvate on Phosphorescent Bacteria. A. Berthelot and G. Amoureux (*Bull. Soc. Chim. biol.*, 1924, **6**, 336—337).—The luminosity of cultures of a species of phosphorescent bacterium (isolated from a marine fish) in a liquid medium was first depressed and afterwards much increased by the addition of sodium pyruvate at the rate of 4 g. per litre. Urea acted similarly, and a still greater effect was obtained with a mixture of urea and pyruvate. It is not yet known whether the pyruvate acts directly on the phenomenon of phosphorescence or whether it simply causes a greater development of the organism. C. T. G.

Culture of Spirochætes in Media containing Sodium Pyruvate. A. Berthelot and P. Séguin (*Bull. Soc. Chim. biol.*, 1924, **6**, 341).—Two species of spirochæte from the mouth—*Sp. dentium* and *Sp. tenuis*—which do not develop on ordinary serum-bouillon, grew and remained alive for more than a month in this medium with the addition of 2 to 10 drops of a 20% solution of sodium or potassium pyruvate to each tube. Such a medium is suitable for the maintenance of pure cultures of these organisms and is much more simple to prepare than Noguchi's medium. C. T. G.

Variations in Hydrogen-ion Concentration during the Assimilation of Ammoniacal Salts of Strong Acids by *Aspergillus repens*, de Bary. D. Bach (*Compt. rend.*, 1924, **178**, 2194—2195).—The growth of this mould is inhibited by high hydrogen-ion concentration, and for this reason a medium containing ammonium chloride is deleterious, since it results in the liberation of hydrochloric acid. Any cause capable of retarding this increase of acidity increases value of the salt as a nutrient for the mould. A. Cousen.

Preparation of Organic Acids by Biological Methods with the Help of Hyphenated Moulds. R. Falck and van Beyma thoe Kingma (*Ber.*, 1924, **57**, [*B*], 915—920).—A general account is given of the experimental technique necessary for the production of uniform results in the investigation of the production of acids from carbohydrates with the aid of moulds. An approximately 1% agar jelly is used as substrate into which the mould hyphæ do not penetrate more than a few millimetres. Dextrose is generally used as source of carbon, but may be replaced by other sugars, glycerol, starch, wood, or cellulose; the best concentration varies greatly with the particular type of mould. Ammonium nitrate

(0·16—0·32%) is the most suitable source of nitrogen; other nutrient salts are required in such small amount that their special provision is unnecessary if technical glucose is employed. For a given solution, the amount of acid formed in the unit of time is proportional within certain limits to the surface of the agar jelly. The production of acids by various types of *Aspergillus*, *Penicillium*, and *Citromyces* has been investigated. The black, brown, or pale brown types of *Aspergillus* yield acid freely, the yellow and greenish-yellow varieties moderately, whereas the pale or colourless types give little acid. The ultimate product is oxalic acid; the intermediate formation of citric acid is nearly always observed.
H. W.

Production of Gluconic Acid by Hyphenated Moulds. R. Falck and S. N. Kapur (*Ber.*, 1924, **57**, [*B*], 920—923; cf. preceding abstract).—Gluconic acid is produced by the action of four varieties of *Aspergillus niger*, *A. cinnamomens*, *A. fuscus*, and *Citromyces lactis* on solutions of glucose in the presence of calcium carbonate. The best conditions are secured by using relatively concentrated sugar and very dilute ammonium nitrate solutions, working at a low temperature, and interrupting the action when the calcium carbonate is dissolved, but previous to the separation of calcium citrate. The yield of acid is 50% of the sugar. The production of glycuronic acid could not be observed.
H. W.

Presence of Pyruvic acid in Cultures of certain *Mucors*. A. Berthelot and R. Pouisot (*Bull. Soc. Chim. biol.*, 1924, **6**, 343—344).—Pyruvic acid was detected in cultures of three species of *Mucor* in media containing sugars, after incubation for 15 days. In older cultures, pyruvic acid was not found. The production of this acid is no doubt one of the factors accounting for the favourable action of *Mucor* on the growth of yeast. C. T. G.

Formation of Pyruvic Acid and Ethyl Alcohol from Calcium Lactate by Yeasts. E. Kayser (*Bull. Soc. Chim. biol.*, 1924, **6**, 345—351).—Further details are given of work already published (cf. A., 1923, i, 986). The formation of the ethyl and amyl esters of acetic and valeric acids by various yeasts in media containing calcium lactate and mineral salts is confirmed. The alcohols were determined after saponification of the distillate from the cultures by a combination of the methods of Duclaux and Nicloux.
C. T. G.

Rôle of the Reaction of the Medium in Selective Fermentation. A. Fernbach and N. Schiller (*Compt. rend.*, 1924, **178**, 2196—2197).—The fermentation of sugar solutions by 8 types of yeast has been studied, and in each case it has been found that lævulose is at first attacked more readily than dextrose, until a point is reached, varying with the yeast employed and not occurring in the case of Sauternes yeast, at which the relative rate of attack is reversed. It was found possible to modify the course of the fermentation in other cases than that of the Sauternes yeast by decreasing the acidity of the solution. A. COUSEN.

Enzymic Equilibria. I. H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **136**, 30—44).—From a mathematical treatment of the results obtained in a study of the equilibria in aqueous systems of the type, methyl alcohol–dextrose–emulsin, and fatty acid–alcohol–lipase, it is concluded that a more satisfactory interpretation results from the assumption that an affinity exists between enzyme and reaction products as well as between enzyme and substrate. This applies even in the case of invertase showing a hydrolytic action only. J. P.

Co-zymase of Yeast. III. H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **136**, 107—129).—The concentration, purification, and characterisation of co-zymase are described. A method has been devised for determining co-zymase, based on the measurement of the carbon dioxide evolved with zymase and dextrose under standard conditions at $p_H=6{\cdot}2$—$6{\cdot}6$. The fermentative power of dried yeast preparations is increased by the addition of co-zymase and also by the addition of washed inactive yeast free from the co-enzyme. The rate of fermentation therefore depends on the relative quantities of zymase and co-zymase, and it is assumed that the two together form a dissociable compound which constitutes the active enzyme. By the addition of either zymase or co-zymase the dissociation of this active compound is suppressed, resulting in an increase in the activity of the mixture. The results on the thermostability of co-zymase are similar to those arrived at by Tholin (A., 1922, i, 305). Co-zymase is decomposed rapidly in solutions more alkaline than p_H 10, shows maximum stability at p_H 7, and is still active in 0·5*N*-hydrochloric acid (p_H 0·6). Contrary to the view hitherto accepted, it was found that lead acetate is capable of precipitating the co-zymase to a greater or less extent according to the p_H of the solution. The co-zymase is not affected by hydrogen sulphide, but is inactivated by traces of lead. When lead acetate was added to yeast juice containing the co-zymase at p_H 6, the free phosphate and the hexosephosphate were precipitated and the co-zymase was found mainly in the filtrate. When the latter was brought to p_H 8·3—10·0 the co-zymase was almost completely precipitated. It could be recovered from the lead precipitate by suitable means and such fractional precipitation may be employed for purification. It can also be purified in a solution free from phosphate, by adsorption on alumina, which is almost quantitative at p_H 10, whilst in acid solutions no adsorption occurs. The alumina adsorbate is strongly active and the co-enzyme is not eluted therefrom by water or very dilute acids although it can be readily eluted quantitatively with 1% phosphate solution at p_H 6·3. D. R. N.

Nitrogen Content of Invertase. K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **136**, 224—231).—In reply to Willstätter and Schneider (this vol., i, 692), it is urged that proportionality between enzyme activity and nitrogen content is possible only when due regard is paid to the inactivation of part of the enzyme during the processes used for its purification. It is shown that, when the same yeast is used and experimental conditions are standardised, an approximate constancy exists for the ratio *If/N*. With simple assumptions, ratios for two of Willstätter's preparations show reasonable agreement.

O. O.

Affinity of Invertase for Different Sugars. III. Identity of Invertase and Raffinase. K. JOSEPHSON (*Z. physiol. Chem.*, 1924, **136**, 62—74; cf. Euler and Josephson, this vol., i, 467; Josephson, this vol., i, 801).—Invertase and raffinase show the same affinity constants to α- and β-dextrose, to lævulose, and to β-galactose, and these sugars inhibit the action of the two enzymes on sucrose and on raffinose to the same extent. It is concluded that invertase and raffinase are identical. Melibiose shows no affinity for invertase. J. P.

Relative Specificity of Yeast Maltase. R. WILLSTÄTTER, R. KUHN, and H. SOBOTKA (*Z. physiol. Chem.*, 1924, **134**, 224—242).—The hydrolysis of α-methyl-, α-ethyl-, and α-phenyl-glucosides and of amygdalin by the maltase of yeasts from various sources was studied. The hydrolysis of α-ethylglucoside in some cases obeyed the law of a unimolecular reaction; in others the rate of reaction fell off more rapidly. In the case of α-phenylglucoside, the curve representing the course of the reaction corresponds with that already described for the hydrolysis of α-methylglucoside (A., 1921, i, 282). The power of different yeast-extracts to hydrolyse the α-glucosides is parallel with their rate of hydrolysis of amygdalin. All the specimens of maltase examined showed less affinity for the aliphatic glucosides than for α-phenylglucoside.

C. R. H.

Lipase of the Castor Oil Bean. R. WILLSTÄTTER and E. WALDSCHMIDT-LEITZ (*Z. physiol. Chem.*, 1924, **134**, 161—223).—The enzyme was most active at a p_H of 4·7 to 5·0; its activity was unaffected by the addition of manganese salts and was inhibited by sodium chloride; the optimum temperature was 35°. An investigation of the kinetics of the reaction under constant physical conditions showed that its course was not regular.

The removal by means of organic solvents of the oil contained in the beans resulted in all cases in a serious loss of enzymic activity; moreover, the preparations so obtained were very unstable. This method of purification was therefore abandoned in favour of the separation, and drying in a vacuum desiccator or in an air current, of the "cream" obtained by centrifuging an aqueous emulsion of the pulverised beans. In this way there was far less loss, especially if the cream were mixed with a quantity of kieselguhr before drying. Further purification was effected by washing the "cream" with dilute alkali. The dried preparation finally obtained retained its activity for a fairly long period; it contained much protein but no carbohydrate. The only marked difference in its elementary composition from that of the crude powdered beans was an increase in the phosphorus content.

The apparent increase in lipolytic activity during germination observed by previous authors (cf. A., 1903, i, 218; 1904, ii, 433) is due to a change in the character of the enzyme by which its optimum hydrogen-ion concentration is shifted to the alkaline side. (For distinction, the original enzyme is termed *spermatolipase*, and the altered one *blastolipase*.) The formation of blastolipase from the spermatolipase can also be brought about by the action of pepsin and by hydrolysis with acids. Dried preparations of blastolipase were much more stable than those of spermatolipase, and their synthetic action, on a mixture of glycerol and oleic acid, was considerably stronger. C. R. H.

Animal Carboxylase. A. Gottschalk (*Biochem. Z.*, 1924, **146**, 582—588).—Rabbit liver pulp to which pyruvic acid is added shows after incubation, both in the presence and in the absence of oxygen, more acetaldehyde formation than controls containing no added pyruvic acid. The presence of a carboxylase is inferred (cf. also Neuberg and Gottschalk, this vol., i, 785). J. P.

Methylated Proteins. I. Action of Proteolytic Enzymes on Methylated Proteins. T. Imai (*Z. physiol. Chem.*, 1924, **136**, 173—187).—When casein or edestin is methylated with methyl sulphate and sodium hydroxide at 20°, the methyl derivative, which is insoluble in alcohol and in ether, is obtained as an amorphous white powder easily soluble in water. These derivatives are hydrolysed by pepsin, trypsin, and erepsin, although to a much lesser extent compared with the unmethylated protein. D. R. N.

Methylated Proteins. II. Hydrolysis of Methylated Casein. T. Imai (*Z. physiol. Chem.*, 1924, **136**, 188—191).—A certain relation exists between the lysin content of a protein and the free amino groups in the protein molecule (cf. A., 1912, i, 1041; 1920, i, 687). If, therefore, methylated amino-acids could be isolated from the products of hydrolysis of a methylated protein, it could be readily ascertained which amino groups are free in the original molecule. Edlbacher (A., 1921, i, 199) obtained in the lysin fraction a considerable quantity of a syrupy mass from which he was not able to isolate any well-defined compound. This fraction has now been further examined. When a methylated protein is hydrolysed with proteolytic enzymes, from the products of hydrolysis histidine is obtained in traces, arginine in a small quantity, whilst a considerable amount is obtained as a syrupy mass in the lysin fraction, from which a crystalline platinum chloride double salt has been isolated. It is very easily soluble in water, and in methyl and ethyl alcohol. D. R. N.

Methylated Proteins. III. Action of Erepsin on Methylated Polypeptides. T. Imai (*Z. physiol. Chem.*, 1924, **136**, 192—204).—It is supposed that in methylated proteins the free amino groups are methylated whilst the imino groups are not affected (A., 1920, i, 825). Owing to the relative difficulty of hydrolysis of methylated proteins by enzymes, it appeared probable that the ease of hydrolysis of the peptide linkings by proteolytic enzymes depended on their distance from the methylated amino groups. To establish this view the behaviour of the betaines of glycylglycine, diglycylglycine, and triglycylglycine towards erepsin has been studied. The first two are not attacked, whilst the latter is hydrolysed to a slight extent. D. R. N.

Action of Erepsin on Benzoylated Polypeptides. T. Imai (*Z. physiol. Chem.*, 1924, **136**, 205—213).—As the methylated polypeptides of glycine are only crystallisable with difficulty, the behaviour of the more easily crystallisable benzoylated polypeptides of glycine towards erepsin has been studied. Benzoylglycylglycine, in common with the methylated dipeptide, is not attacked whilst the benzoyl-di-, -tri-, and -tetra-glycylglycines are hydrolysed to different extents. It is uncertain which peptide linkings in these derivatives are attacked. D. R. N.

Comparison of certain Oxidising Enzymes of the Higher and Lower Plants. M. E. Robinson (*Biochem. J.*, 1924, **18**, 543—548).—The oxydases of the higher plants consist of three components, a pyrocatechol derivative and two enzymes—oxygenase and peroxydase. Those of the *Basidiomycetes* consists only of an enzyme-like peroxide and peroxydase. The experiments of Onslow on certain phanerogam oxydases and those of Gallagher on extractable plant phosphatides have been repeated and confirmed. Gallagher's interpretation of his results is criticised. S. S. Z.

Oxidising Enzymes. VII. Oxygenase of Higher Plants. M. W. Onslow (*Biochem. J.*, 1924, **18**, 549).—Polemical. It is reasserted that oxygenase catalyses the formation of peroxide; Gallagher's assertion that the blueing of guaiacum is due to the presence of an autoxidisable lecithin-like substance is criticised.
S. S. Z.

Use of Guaiacol for Measuring the Activity of Oxydase Preparations. P. Fleury (*J. Pharm. Chim.*, 1924, [vii], **29**, 402—414).—Tetraguaiacoquinone, $[C_6H_3(OMe)O—]_4$, to which the red coloration given by the action of laccase on guaiacol is due, separates as a precipitate when the solution is kept and forms colloidal solutions, which readily coagulate, with water. It can be used for the purposes of colorimetric analysis, however, by extracting it with chloroform and comparing the colour of the solution with that of a 0·01*N*-solution of iodine. A solution of 46·5 mg. of guaiacoquinone in 1 litre of chloroform, obtained by extraction from aqueous solution, has the same colour as 0·01*N*-iodine solution, the thickness of the layer viewed in each case being 10 mm. The oxidation of guaiacol by air in the presence of laccase proceeds quantitatively, but the yield of guaiacoquinone varies between 72 and 95%, being influenced adversely by allowing the reaction to be prolonged, by the presence of an excess of guaiacol, by the alkalinity of the medium, and by raising the temperature. These influences are negligible, however, under the conditions of the experiments described. The activity of the laccase remains practically unchanged at the end of the reaction. W. T. K. B.

Influence of X-Rays on Leucocytic Oxydases. P. Lemay, C. Guilbert, R. Petit, and L. Jaloustre (*Compt. rend.*, 1924, **178**, 1711—1713; cf. Maubert and others, A., 1923, i, 723; this vol., i, 808).—The activity of both direct and indirect leucocytic oxydases is increased by weak doses of X-rays, but whilst the direct oxydases remain stable and unchanged under the action of more powerful doses, the indirect oxydases are inactivated. The latter are not, however, destroyed, and they recover again a certain time after the cessation of radiation. M. S. B.

History of Carbon Dioxide Assimilation. F. Weigert (*Z. physikal. Chem.*, 1924, **109**, 79—80; cf. A., 1923, i, 1271).—A question of priority (cf. Warburg and Negelein, this vol., ii, 241). M. S. B.

Blackman's Reaction. O. Warburg and T. Uyesugi (*Biochem. Z.*, 1924, **146**, 486—492).—Using suspensions of the alga *Chlorella*, the influence of hydrogen cyanide and of various substituted urethanes on the Blackman reaction (rate of decomposition of carbon dioxide and liberation of oxygen in strong light), on the one hand, and on the decomposition of hydrogen peroxide and on respiration on the other, has been investigated. The parallelism between the two sets of results lends support to the views of Willstätter and Stoll ("Untersuchungen über die Assimilation der Kohlensäure," Berlin, 1918). J. P.

Influence of Acidity on Plant Growth without regard to other Factors. A. G. McCall (*J. Amer. Soc. Agron.*, 1923, **15**, 290—297).—A general review of recent work on soil reaction and the tolerance of acidity by plants in solution cultures and by bacteria in soils. Measurements of hydrogen-ion concentrations may prove more useful than lime requirement tests, but in practice the application of lime need not necessarily be carried to the point of neutralisation. E. M. C.

Effect of Hydroxyl-ion Concentration on the Growth of Walnut Roots. H. S. Reed and A. R. C. Haas (*Amer. J. Bot.*, 1924, **11**, 78—84).—Walnut seedlings are very sensitive to the absence of calcium from the culture solution. The injury to walnut roots from solutions of high p_H values is due principally to calcium starvation rather than to the effect of high concentration of hydroxyl ions on the plant. A. A. E.

Effect of Salts on the Intake of Inorganic Elements and on the Buffer System of the Plant. D. R. Hoagland and J. C. Martin (*California Agr. Expt. Sta., Tech. Paper*, 1923, 8, 26 pp.).—Sodium chloride and sodium sulphate, added to a culture solution, caused marked alteration in the composition of the barley plant, tending to decrease the absorption of calcium, magnesium, and potassium. Sodium and chlorine may be absorbed and stored by the barley plant in relatively large quantities. The sulphate ion is taken up by several plants less rapidly than the chloride ion. No definite alkali tolerance for different plants can be established because of the important modifying effects of environmental factors. The buffer effects of the expressed sap of stems and leaves was greater than that of roots. Rapid and extreme changes in reaction of the expressed root sap were caused by the addition of sodium hydrogen carbonate to the culture solutions. Calcium chloride produced appreciable changes in the reaction and buffer effects of plant juices. Sodium nitrate increased the alkalinity of the expressed root sap, with a slight accompanying injury resembling that induced by sodium hydrogen carbonate. E. M. C.

Effect of Sodium Chloride and Calcium Chloride upon Growth and Composition of Young Orange Trees. H. S. Reed and A. R. C. Haas (*California Agr. Expt. Sta., Tech. Paper*, 1923, 4, 21 pp.).—Orange trees were grown in various nutrient solutions in sand and the distribution throughout the plant of nitrogen, calcium, sodium, and potassium was determined. Physiological disturbances developed in a few months in the trees grown in incomplete nutrient solutions. Omission of calcium caused spotting and shedding of the leaves and the repeated development of new buds. In such trees, the calcium was retained principally in the trunks and roots, and was present only in small amounts in the leaves, shoots, and rootlets, indicating a low mobility of calcium. In plants grown in full nutrient solutions, the percentage of calcium in the ash was fairly constant throughout the plant. The percentage of potash was high in all parts of the trees. In the presence of calcium chloride vigorous growth was made even when considerable amounts of sodium chloride were also present. E. M. C.

Nutrition of the Potato Plant with Special Reference to Water Cultures. W. Newton (*J. Amer. Soc. Agron.*, 1923, **15**, 392—399).—Potato plants were rapidly injured by the omission of calcium salts from the solution, but showed an increased yield of tubers when potassium was omitted. It is suggested that the value of potash fertilisers may be due in part to the indirect effect of increasing the calcium content of the soil solution. E. M. C.

Plant Colloids. XV. Amylopectins Prepared from Different Starches. M. Samec, M. Minaeff, and N. Ronžin (*Koll. Chem. Beihefte*, 1924, **19**, 203—212).—Amylopectins of various origin differ in the appearance, conductivity, viscosity, and hydrogen-ion concentration of the aqueous solutions, and in the phosphorus content, titratable acidity, and amount of alkali combined with one g.-atom of phosphorus. The amylopectins from underground storage organs (potato, arrowroot, and tapioca) and from seeds (maize, rice, wheat) form two distinct groups. These differences do not depend on variations in the cations associated with the amylophosphoric acids, since they are maintained in starches washed with dilute hydrochloric acid. Synthetic amylopectins prepared from the different starches are closely analogous.

E. M. C.

Occurrence of Alkaloids in Nature. I. Common Occurrence of Alkaloids and Tannides. L. Rosenthaler and M. Mosemann (*Schweiz. Apoth.-Ztg.*, 1924, **62**, 13—15, 29—31, 48—50; from *Chem. Zentr.*, 1924, i, 1678).—In a considerable number of cases alkaloids and tannides occur together in the same cells. It is not, however, always necessary to assume the existence of alkaloid–tannide compounds. Such compounds may be present where the presence of alkaloids is not shown by the usual tests. Many alkaloids and tannides are products of excretion and insoluble alkaloid–tannide compounds may also be regarded as such. They may, however, have some physiological function. G. W. R.

Phytosterols of the Endosperm of Corn [Maize]. R. J. Anderson (*J. Amer. Chem. Soc.*, 1924, **46**, 1450—1460).—Maize gluten (23 kg.) was extracted with ether-alcohol (1 : 1), and the extract, which contained some free phytosterol, yielded, on hydrolysis with alcoholic potassium hydroxide, crude, crystalline phytosterol (55 g.) and an oil (30 g.). *Dihydrositosterol*, $C_{27}H_{47}OH,H_2O$, m. p. 139° (anhydrous, m. p. 141°), $[\alpha]^{20}_{D}$ $+24{\cdot}23°$ in chloroform, was obtained from the crude phytosterol by 39 crystallisations from alcohol, and hydrolysis of the purified *acetyl* derivative, which formed large hexagonal plates, m. p. 138°, $[\alpha]^{20}_{D}$ $+14{\cdot}41°$. The accompanying sitosterol could not be completely removed by crystallisation, but was extracted from the chloroform solution of the acetyl derivatives by concentrated sulphuric acid, dihydrositosterol then being obtained of $[\alpha]^{20}_{D}$ $+25{\cdot}04°$. The crude phytosterol (15·6 g.) obtained similarly from maize bran (15 kg.) is relatively rich in dihydrositosterol. Dihydrositosterol does not give the Liebermann-Burchard reaction, and does not absorb bromine. F. G. W.

Aleurone Cells of Cereals. E. B. Bennion (*Cereal Chem.*, 1924, **1**, 138—148).—The author has separated the aleurone layer from barley and wheat, and made elementary analyses on products obtained by extraction with sodium chloride solution and alcohol. The aleurone cells of barley contain only small quantities of fatty matter, but those of wheat contain an oil and a white, waxy material, probably phytosterol. The residue after extraction with alcohol was rich in nitrogen and ash. E. M. C.

The Genus *Mentha*. *Mentha piperita*. F. J. Bacon, G. C. Jenison, and R. E. Kremers (*J. Amer. Pharm. Assoc.*, 1923, **12**, 1075—1077).—Methyl*cyclo*hexanone is not constantly present and it is possible that its reported occurrence is due to the treatment to which the oil was subjected. Its precursor, pulegone (and possibly piperitone) is constantly present. It is suggested that menthenone is first formed and that menthol and menthone are formed from it by reduction. Aldehydes are present in only small proportions in the natural oil and are mostly eliminated in the refining processes. From 5454·5 kg. of oil, 500 g. of *iso*valeraldehyde were obtained. Chemical Abstracts.

Constituents of Ragweed Pollen. F. W. Heyl (*J. Amer. Pharm. Assoc.*, 1923, **12**, 669—676; cf. A., 1922, i, 1224).—The ethereal extract of ragweed pollen contained formic, acetic, valeric, lauric, oleic, linoleic, palmitic, and myristic acids, and an unsaturated acid, $C_{10}H_{18}O_2$; the alcoholic extract contained a mixture of phosphatides. The acetone-insoluble lipin was obtained by recrystallisation. The water-soluble portion of the alcoholic extract contained adenine, betaine, sucrose, lævulose, and a trace of guanosine. With the exception of the colouring matters and possibly a proteose, none of the 27 substances isolated appears to be a chemical specialisation of the pollen cell. CHEMICAL ABSTRACTS.

Accumulation of Iron and Aluminium Compounds in Maize Plants and its Probable Relation to Root Rots. II. G. N. HOFFER and J. F. TROST (*J. Amer. Soc. Agron.*, 1923, **15**, 323—331).—The accumulation of iron and aluminium compounds in the nodal tissues of maize plants is affected by soil conditions. The accumulation of aluminium and to a less extent of iron in the plants is associated with retarded growth and increased susceptibility of certain strains to root rots. E. M. C.

Action of Metabolic End-products on Plants. III. Action of Nitrogen-free End-products of Plant Metabolism (Ethereal Oils, Terpenes, etc.) on the Germination of Seeds. W. SIGMUND (*Biochem. Z.*, 1924, **146**, 389—419).—An investigation of the influence of various ethereal oils and terpenes on the germination of vetch, wheat, and rape seeds. Mustard oil proved most toxic, followed by clove and caraway oil; the oils of aniseed, fennel, geranium, peppermint, rosemary, and thyme, although less active than the first three, also definitely inhibited germination. Oil of garlic was toxic in the form of vapour but much less so in solution, whilst oil of turpentine gave similar results. The oils of bergamot, cedar, citron, eucalyptus, rue, and juniper berry were practically devoid of effect in solution. The results obtained with individual constituents of the oils were as follows: Hydrocarbons:—cymene, *d*- and *l*-limonene, *d*- and *l*-pinene, and styrene, no action. Alcohols:—borneol, linaloöl, menthol, terpin hydrate, no action; terpineol, toxic. Aldehydes:—benzaldehyde, citral, cinnamaldehyde, very toxic; anisaldehyde, somewhat less toxic; *iso*valeraldehyde and vanillin least toxic. Ketones:—in order of diminishing toxicity, carvone, camphor, fenchone, cineole. Phenols:—carvacrol, thymol, apiole, safrole, very toxic; anethole, weakly toxic. Acid:—anisic acid, little or no action. Ester:—methyl salicylate, toxic. J. P.

Action of Formates on the Growth of certain Plants in Pot Cultures. C. RICHET, junr. (*Compt. rend.*, 1924, **178**, 1922—1923).—The addition of small amounts of sodium or calcium formate to soil, either at the time of sowing or at the commencement of germination, increased the germinating power of wheat and barley by 10—20%. There was no significant increase in the weight of the shoots. E. M. C.

Influence of Temperature of the Soil on the Relation of Roots to Oxygen. CANNON (*Science*, 1923, **58**, 331).—The maximum, optimum, and minimum temperatures for the growth of roots in normally aërated soil are altered under conditions of diminished oxygen supply. The rate of root growth with a given oxygen supply as compared with the rate under normal aëration decreases with increase of temperature of the soil.

Typical results are given with regard to several species of plants, and it is suggested that investigations on the oxygen relation of roots would give results of considerable value from an ecological point of view. C. T. G.

Action of Salt Solutions on the Soil. II. O. Nolte and E. Sander (*Landw. Versuchs-Stat.*, 1924, **102**, 219—225).—On theoretical grounds and as the result of earlier work (cf. A., 1921, i, 914), it was expected that the rate of percolation of a salt solution through a column of soil, *i.e.*, the permeability of the soil, would bear a definite relation to the reaction of the solution. Tables and graphs are presented showing the changes in the p_H values (determined electrometrically), week by week, of the percolate from a column of soil, treated for 4 weeks with water, followed by a 1% salt solution for 4 weeks and then by water again for a final period. Uni-, bi-, and ter-valent salts (chlorides) are included. A close connexion between the hydrogen-ion concentration and the permeability is indicated. Similar changes in reaction were recorded on percolating powdered quartz with potassium chloride solution. C. T. G.

Formation of Sodium Carbonate in Soils. A. B. Cummins and W. P. Kelley (*California Agr. Expt. Sta., Tech. Paper*, 1923, 3, 35 pp.).—An explanation is suggested for the observation that semi-arid soils, on treatment with sodium chloride solutions and subsequent leaching, swell and become impervious, yielding a dark, alkaline percolate. The sodium silicate complexes ("absorbates") formed by the displacement of calcium and other bases by sodium are less stable, more soluble, and more readily hydrolysed than the corresponding calcium complexes. The alkalinity results from the hydrolysis of these "absorbates" on the reduction of the salt concentration by leaching and an interaction with the carbon dioxide of the soil solution. Some of the products of hydrolysis tend to assume the colloidal state. The presence of calcium carbonate is not essential for the formation of sodium carbonate in soils. Certain soils from humid regions react similarly to, but not so markedly as, the semi-arid soils. Alkalinity was also developed by granite and pure mineral silicates after similar treatment. Sodium chloride solutions more concentrated than $0{\cdot}01N$ were able to form hydrolysable compounds in soil, and the concentration of sodium chloride needed to be reduced to about one-half by leaching before alkalinity developed. Calcium salts in sufficient concentration prevented the formation of hydrolysable sodium "absorbates," and tended to prevent the hydrolysis of such compounds when already formed. E. M. C.

Removal of Sodium Carbonate from Soils. W. P. Kelley and E. E. Thomas (*California Agr. Expt. Sta., Tech. Paper*, 1923, 1, 23 pp.).—Active oxidation of added sulphur took place in alkali soils containing relatively high concentrations of sodium salts and ultimately removed the soluble carbonates in all but one of the soils studied. Calcium sulphate reduced the soluble carbonates, but failed to remove the alkalinity except when it was used in conjunction with leaching. Sulphuric acid was somewhat more effective than the sulphur oxidation products and considerably more so than calcium sulphate. The amounts of these materials needed is considerably greater than the soluble carbonate content, indicating that they interact with silicates and other alkaline compounds. In view of the importance of the subsoil, treatment with calcium sulphate followed by leaching seems to be the most successful for black alkali soils. Preliminary experiments indicated that ferrous sulphate and alum might also prove useful. E. M. C.

Alkali Soil Investigations. I. Colloidal Phenomena. J. S. JOFFE and H. C. MCLEAN (*Soil Sci.*, 1924, **17**, 395—409).—The oxidation of sulphur added to an alkali soil resulted in an increased surface tension of the aqueous extracts, and increased rates of capillary rise of water and percolation of water through the soil. E. M. C.

Importance of Hydrogen-ion Concentration Control in Physico-chemical Studies of Heavy Soils. R. BRADFIELD (*Soil Sci.*, 1924, **17**, 411—422).—The amount of electrolyte required to flocculate a colloidal clay solution can only be defined with reference to a definite p_H value. The initial reaction of the clay is an important factor in determining its behaviour at other p_H values; with alkaline flocculants, a part is utilised in neutralising an acid clay and the concentration of the clay thus becomes important. Different acids flocculate colloidal clay solutions at about the same concentration of hydrogen ions, but the amounts of acid needed may vary widely if expressed in terms of the titratable acidity. The hydrogen-ion concentration at equilibrium plays an important part in determining the absorption and exchange of bases between clay and salts. A colloidal clay was treated with various mixtures of potassium chloride and hydroxide, such that the potassium was $0{\cdot}1N$. The amount of potassium absorbed increased steadily with the p_H value. The amounts of alumina, silica, and ferric oxide liberated decreased with decreasing hydrogen-ion concentration, and became negligible near the neutral point. With increasing alkalinity, silica and alumina were again made soluble. The amounts of calcium and magnesium oxides liberated fell off with decreasing acidity and remained negligible in the more alkaline solutions. The difference between the absorption and liberation of bases, expressed in equivalent amounts, closely followed the equilibrium p_H value over a wide range and became zero for the value corresponding with that of the original clay solution. E. M. C.

Active Acidity of Soils. E. T. WHERRY (*J. Wash. Acad. Sci.*, 1924, **14**, 207—211).—A restatement of the importance of the measurement of the hydrogen-ion concentration or "active acidity" of soil suspensions. E. M. C.

Methods of Diagnosing [Soil] Toxicity. P. L. Gile (*J. Amer. Soc. Agron.*, 1923, **15**, 305—312).—The author reviews the experiments on the relationship of aluminium salts to soil acidity. It is suggested that no specific toxicity of aluminium ions has been established and that the importance of the soil reaction is connected with its effect on the availability of different nutrients.

E. M. C.

Inorganic Substances, especially Aluminium, in Relation to the Activities of Soil Micro-organisms. Whiting (*J. Amer. Soc. Agron.*, 1923, **15**, 277).—A discussion of recent American work on the part played by aluminium in the occurrence of acidity and toxicity in soils and its influence on the biological activity of soil organisms. A summary of "concordant results" and of "results in need of verification and further investigation" is included.

C. T. G.

Effect of certain Potassium Fertilisers on Ammonification, Nitrification, and Crop Production. Vaudecaveye (*J. Amer. Soc. Agron.*, 1923, **15**, 415).—An account of pot-culture experiments on the effects of organic manure, lime, kainit, and potassium chloride and sulphate on ammonification, nitrification, and crop yield. Potassium fertilisers caused large increases in nitrification, but had little effect on ammonification. A definite relationship is shown to exist between bacterial activities and the production of soluble potassium in the soil.

C. T. G.

Microbiological Analysis of Soil as an Index of Soil Fertility. VIII. Decomposition of Cellulose. S. A. Waksman and O. Heukelekian (*Soil Sci.*, 1924, **17**, 275—291).—There is a definite relation between the amount of cellulose decomposed in the soil by micro-organisms and the nitrogen assimilated, the available nitrogen becoming the controlling factor. Differences in the amount of cellulose decomposed in soils of different fertility are due to differences in the availability of the nitrogen and not to variations in the micro-flora, since all soils contain organisms able to attack cellulose. In acid soils the fungi are chiefly concerned, whilst in limed and neutral soils bacteria and probably actinomycetes also play an active part.

The cellulose-decomposing power of a soil determined with and without addition of sodium nitrate and with and without addition of calcium carbonate and mineral salts can be used to assist in the differentiation of soil fertility. The breaking down of cellulose (finely-divided filter-paper) may be followed by measuring the carbon dioxide evolved during a given time; or, the residual cellulose in the soil after incubation may be determined by the use of Schweitzer's reagent according to the method of Charpentier (*Diss.*, Helsingfors, 1921). Detailed procedures are suggested.

C. T. G.

Organic Chemistry.

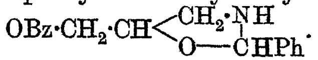
Photolysis of Organic Iodides: The Photochemical Threshold and Energy of Linking. A. Job and G. Emschwiller (*Compt. rend.*, 1924, **179**, 52—54).—The action of light on ethyl iodide in a closed system and in complete absence of oxygen results in the liberation of iodine and of a large quantity of gas composed principally of ethylene and ethane, together with small amounts of butane and hydrogen. The presence of butane is readily explained by the assumption of a unimolecular decomposition, and that of ethylene and ethane, which is often observed when an ethyl radical is set free, is attributed by Schlubach and Goes (A., 1922, i, 1204) to a lack of equilibrium in the ethyl radical which causes migration of one of its hydrogen atoms to a neighbouring radical. Since, however, ethylenic hydrocarbons are never found in the gas resulting from the photochemical decomposition of alcohols, aldehydes, acids, or ketones, the iodine from the ethyl iodide probably acts as acceptor towards a hydrogen atom of the ethyl radical, ethylene and hydrogen iodide being first formed and the latter then being decomposed under the influence of light. Results similar to the above are observed with methyl iodide.

If the iodine in ethyl iodide is represented as united to the carbon by means of a co-valence, the quantum of luminous energy which detaches the iodine from the molecule must bring the latter to an energy level at least equal to the critical level. If it touches and just suffices to bring to the critical level an average molecule, this quantum, $h\nu$, will by definition be the critical complement and measures the energy of linking of the co-valence, C—I. When a tube containing ethyl iodide is placed in the spectrum of the carbon arc, the reaction appears distinctly as soon as wave-lengths shorter than 0·41 μ are reached and increases in intensity as the frequency increases (cf. Crymble, Stewart, and Wright, A., 1910, ii, 470). The energy quantum corresponding with this wave-length is 69,300 cals. per g.-mol., which is thus approximately the energy of the carbon–iodine co-valence in ethyl iodide. T. H. P.

Oxonium Compounds. Researches on the Relative Strength of the Higher Valencies of Oxygen in different Classes of Organic Compounds. M. W. Tschelinzeff (*Bull. Soc. chim.*, 1924, [iv], **35**, 741—753).—The relative strength of the higher valencies of oxygen has been determined by measurements of the heats of formation of a large number of additive compounds of magnesium ethoxy iodide, EtO·MgI, with different classes of organic compounds. Among oxonium compounds of the hydrone type, $R_2O<$, such as those obtained from alcohols, phenols, and ethers, the strength of the additional oxygen valencies depends closely on the radicals attached to the oxygen, but with the carbonyl oxonium compounds, $R_2CO<^{\cdot\cdot}_{\cdot\cdot}$, formed by ketones and aldehydes this influence is less marked, and the thermal effects of the addition of magnesium ethoxy iodide are more constant, maintaining their value even with aromatic radicals. The number of molecules of the organic compound combining with 1 mol. of magnesium ethoxy iodide varies from one to three, the thermal effects of the addition of the second and third molecules being smaller than that produced by the first. With the aliphatic radicals, the largest thermal effects are produced by the first members of the series. Aromatic radicals usually produced a marked lowering of the heats of formation. Among the alcohols, the strongest thermal effects were produced with the primary alcohols and the smallest by the tertiary alcohols, the effects produced by phenols being of the same magnitude as in the case of tertiary alcohols. With oxonium compounds of a mixed hydrone–carbonyl type, such as those formed by esters, the thermal effects are produced by the carbonyl oxygen, and correspond with those observed with the compounds produced from ketones. No thermal effect was observed with furan, pyrrole, or thiophen compounds, the higher valencies in these compounds falling to zero. The formation of oxonium compounds from dimethylpyrone is due to the carbonyl oxygen, as is shown by a comparison of the thermal effects produced with magnesium ethoxy iodide and dimethylpyrone, furan, and quinone. Oxygen in a ring compound shows very little higher valency. In some cases, the molecules attached to magnesium ethoxy iodide can be displaced either partly or completely by other molecules. Thus ethyl alcohol replaces phenol: $ROMgI,3PhOH+3EtOH=ROMgI,3EtOH+3PhOH$. The course of the reaction depends partly on the nature of the original oxonium complex and partly on the radicals bound to it. The displacements always follow the relative value of the heats of formation of the respective complexes. R. B.

Physical–Chemical Properties of Mixtures of Ethyl and *n*-Propyl Alcohols. G. S. PARKS and J. R. SCHWENCK (*J. Physical Chem.*, 1924, **28**, 720—729).—Mixtures of ethyl and *n*-propyl alcohols form an almost "ideal" system. The heat evolution on mixing is very small (<5 cals. per mol. of mixture); the densities and refractive indices agree well with those calculated on the assumption of ideal solution. The vapour pressures of the mixtures are slightly higher than those calculated from Raoult's law, and the viscosities deviate about 2% from the values found by Kendall's equation (A., 1920, ii, 670). The entropy change due to mixing is almost identical with that calculated on the assumption of ideal solution. S. K. T.

Synthesis and Structure of Glycerides. M. BERGMANN (*Z. physiol. Chem.*, 1924, **137**, 27—46; cf. A., 1921, i, 444; Fischer, Bergmann, and Bärwind, A., 1920, i, 805).—A method is described for the synthesis and determination of structure of α-monoglycerides, and incidentally of αβ-diglycerides. The initial material, γ-chloro-β-hydroxypropylamine, may be condensed with benzaldehyde, yielding 2-phenyl-5-chloromethyloxazolidine. The imino group of the latter is then acylated (for example, with benzoyl chloride) and on removal of the benzaldehyde residue by acid hydrolysis, there is obtained a compound of the type of γ-chloro-β-hydroxy-α-benzoylaminopropane. On boiling the latter with water, a replacement of the chlorine by hydroxyl occurs, simultaneously with an intramolecular change, giving γ-aminopropyleneglycol α-benzoate hydrochloride, which is converted into glycerol α-benzoate. The structure of the latter is proved by *p*-nitrobenzoylation of its free hydroxyl groups, and its identity with that prepared by Fischer, Bergmann, and Bärwind (*loc. cit.*) from *iso*propylideneglycerol. The intermediate compounds of the type of γ-aminopropyleneglycol α-benzoate may be used for a new synthesis of αβ-diglycerides. For this purpose, the initial substance is condensed with benzaldehyde, resulting, in this particular instance, in the formation of 2-phenyl-5-benzoxymethyloxazolidine,



$$OBz{\cdot}CH_2{\cdot}CH\begin{matrix}\diagup CH_2{\cdot}NH\\ \diagdown O\text{—}CHPh\end{matrix}.$$

This, on benzoylation or *p*-nitrobenzoylation and subsequent hydrolysis as before to remove the benzaldehyde residue, gives a substance of the type of γ-benzoylaminopropyleneglycol α-benzoate. This yields, on treatment with phosphorus pentachloride and subsequently with water, by intramolecular change, γ-aminopropyleneglycol αβ-dibenzoate, whence glycerol αβ-dibenzoate is obtained as usual.

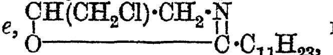
Glycerol αβ-*dibenzoate*, previously known only as an oil, has been obtained as a colourless solid, m. p. 57—58°. 2-*Phenyl*-5-*benzoxymethyloxazolidine* (preparation above), m. p. 76°, yields a p-*nitrobenzoyl* derivative, m. p. 95—96°. The resolution of γ-aminopropyleneglycol αβ-dibenzoate, previously effected through the quinate, has been carried out anew, by condensation of the base with helicin. There crystallises out a yellow *Schiff's base*, m. p. 175—176°, $[\alpha]_D$ −46° (in glacial acetic acid). From this compound, the *l*-amine hydrochloride is obtained in an almost pure form. In anticipation of future syntheses of glycerides, a number of other substances were prepared. 2-*Phenyl*-5-*chloromethyloxazoline*, m. p. 25°, b. p. 120—123°/1 mm., is obtained by the action of sodium acetate on its *hydrochloride*, which results from the action of thionyl chloride on γ-chloro-β-hydroxy-α-benzoylaminepropane.

[With F. WEINMANN.]—γ-*Iodo*-β-*hydroxy*-α-*benzoylaminopropane*, m. p. 138—139°, is obtained from the corresponding chloro compound by the action of sodium iodide; it gives, on boiling with water, γ-*aminopropyleneglycol* α-*benzoate hydriodide*, and on treatment with stearyl chloride, γ-*iodo*-β-*stearoxy*-α-*benzoylaminopropane*. The latter on successive treatment with phosphorus pentachloride, alcohol, and hydrochloric acid, gives γ-*iodo*-β-*stearoxypropylamine hydrochloride*, needles, m. p. 90—93°.

[With P. ECKWALL.]—γ-*Iodo*-β-*lauroxy*-α-*benzoylaminopropane*, m. p. 50—51°, gives, on boiling with silver nitrite, a γ-*benzoylaminopropyleneglycol monolaurate*, m. p. 79—80°.

[With E. Brand and F. Dreyer.]—*γ-Laurylaminopropyleneglycol α-laurate*, m. p. 82—83°, is obtained by the action of lauryl chloride on 2-phenyl-5-hydroxymethyloxazolidine, and the usual hydrolysis; with palmityl chloride it yields *γ-laurylaminopropyleneglycol α-laurate β-palmitate*, m. p. 55—56°. *γ-Laurylaminopropyleneglycol αβ-dilaurate*, m. p. 47—49°, is prepared from γ-aminopropyleneglycol and lauryl chloride. It yields, on treatment with phosphorus pentachloride and subsequently alcohol and oxalic acid, *γ-aminopropyleneglycol αβ-dilaurate hydrogen oxalate*, m. p. 134° after softening at 104°. The corresponding *hydrochloride* is described. *γ-Aminopropyleneglycol α-laurate β-palmitate hydrogen oxalate*, no definite m. p., may be obtained from *γ-laurylaminopropyleneglycol α-laurate β-palmitate* in the usual manner. *γ-Palmitylaminopropyleneglycol α-palmitate*, m. p. 90—91°, is prepared from 2-phenyl-5-hydroxymethyloxazolidine in the usual way. *γ-Palmitylaminopropyleneglycol α-palmitate β-laurate*, needles, m. p. 56—59°, is converted into *γ-aminopropyleneglycol α-palmitate β-laurate hydrogen oxalate*. B. F.

α-Monoglycerides of Fatty Acids of High Molecular Weight. M. Bergmann and S. Sabetay (*Z. physiol. Chem.*, 1924, **137**, 47—61; cf. preceding abstract).—Attempts are described to establish further the constitution of certain glycerides containing an asymmetric carbon atom by isolating their optically active forms. It is found that the optical activity is somehow masked by the presence of hydroxyl groups and becomes evident only when these are more or less replaced, for instance, by solution in thionyl chloride. A similar masking effect is observed with complex fatty acyl groups.

γ-Chloro-β-hydroxy-α-laurylaminopropane, m. p. 54—55°, is prepared from 2-phenyl-5-chloromethyloxazolidine by the usual method (see preceding abstract). On treatment with thionyl chloride, it yields the *hydrochloride* of *2-undecyl-5-chloromethyloxazoline*,  $\begin{array}{l}\mathrm{CH(CH_2Cl)\cdot CH_2\cdot N}\\ \mathrm{O{-\!-\!-\!-\!-\!-\!-}C\cdot C_{11}H_{23}}\end{array}$, m. p. 96—98°, which on hydrolysis gives the free oxazoline. The oxazoline hydrochloride is easily soluble in mineral acids, which, especially on warming, give rise to an intramolecular change, yielding *γ-chloro-β-lauroxypropylamine hydrochloride*, m. p. 86—87°. *γ-Iodo-β-hydroxy-α-laurylaminopropane*, m. p. 55—56°, is prepared by boiling the corresponding chloro compound with sodium iodide. *γ-Aminopropyleneglycol α-laurate hydrochloride* is prepared by heating γ-chloro-β-hydroxy-*N*-laurylpropylamine with excess of water; if the reaction is carried out in the presence of 1 mol. of potassium hydroxide, to neutralise the acid formed, a *compound*, $C_{15}H_{29}O_2N$, of m. p. 75—76° is isolated. γ-Aminopropyleneglycol α-laurate condenses with benzaldehyde to give *2-phenyl-5-lauroxymethyloxazolidine*, m. p. 62°. This may be stearylated, and on fission in the usual way gives *γ-stearylaminopropyleneglycol α-laurate*, m. p. 98°. γ-Aminopropyleneglycol α-laurate, on treatment with alkali, yields by intramolecular rearrangement *γ-laurylaminopropyleneglycol*, m. p.

99—100°. The resolution of inactive γ-aminopropyleneglycol α-laurate into its active components is effected by fractionally crystallising its acid saccharate, whereby d-γ-*aminopropyleneglycol α-laurate hydrochloride*, $[\alpha]_D^{18}$ +12·4° in absolute alcohol, is obtained. By the usual means, an attempt was made to convert the *d*-amine into an optically active α-monolaurin, the product had m. p. 62—63°, and showed no optical rotatory power in indifferent media, but was lævorotatory in thionyl chloride. *dl*-α-Monolaurin under similar conditions gave an inactive product.

γ-*Chloro*-β-*hydroxy*-α-*stearylaminopropane*, rhombic plates, m. p. 77—77·5°, is prepared like its lauryl analogue, and on boiling with water gives γ-*aminopropyleneglycol α-stearate hydrochloride*, which shows remarkable colloidal properties on treatment with water. The benzaldehyde condensation product of the above amine is 2-*phenyl*-5-*stearyloxymethyloxazolidine*, m. p. 80°, whilst the hydrochloride of the amine, on treatment with 1 mol. of very dilute alkali, gives, by internal rearrangement, γ-*stearylaminopropyleneglycol*, m. p. 105°. The fission of γ-aminopropyleneglycol α-stearate into its optically active components is carried out as in the case of its lauryl analogue, and there is finally obtained a d-γ-*aminopropyleneglycol α-stearate hydrochloride*, $[\alpha]_D^{41}$ +10·5°. This was converted into an α-*monostearin*, which showed no optical activity in the usual solvents, but was lævorotatory in thionyl chloride.

B. F.

Trimyristin, a Glyceride present in Milk. M. Piettre and C. Roéland (*Compt. rend.*, 1924, **178**, 2283—2285).—The cream from 500 c.c. of milk is stirred with 200 c.c. of a mixture of alcohol (1000 parts by vol.) and ether (1100 parts by vol.), and a further 50—60 c.c. of ether are added subsequently. The ether–alcohol extract is filtered and allowed to evaporate slowly at 8—10°. Trimyristin crystallises from the solution in long plates, m. p. 52—54°. It gives myristic acid, m. p. 50—52°, when hydrolysed with alcoholic potassium hydroxide. The calculated content of the glyceride is 2—2·4 g. per litre of milk. It is less easy to obtain a pure product from butter.

W. T. K. B.

Dependence of Rotatory Power on Chemical Constitution. XXII. Some Compounds containing the Secondary Octyl Radical Linked to Oxygen. H. Hunter (*J. Chem. Soc.*, 1924, **125**, 1389—1395).—The complex rotatory dispersion associated with the carboxyl group or its equivalents is considered to be due to the presence in one molecule of both a singly- and a doubly-linked oxygen atom, arranged unsymmetrically. Exceptions in the case of the β-octyl compounds are the carbonates and sulphite. It is suggested that in these cases the unsaturated oxygen atoms are distributed symmetrically about the unsaturated one, and that this is sufficient to suppress any obvious complexity of rotatory dispersion. The following compounds are described: *Di*-d-β-*octylformal*, $CH_2(OC_8H_{17})_2$, mobile liquid with fragrant odour, b. p. 175—177°/16 mm., d_4^{17} 0·8523, $n_D^{20·6}$ 1·4314; d-β-*octyl chloroformate*, $C_8H_{17}·O·COCl$, made by the action of carbonyl chloride on *d*-β-octanol in pyridine, b. p. 92°/13 mm., d_4^{19} 0·9748, n_D^{20} 1·4282; *ethyl* d-β-*octyl carbonate*, $EtO\cdot CO\cdot OC_8H_{17}$, made by the action of ethyl alcohol on the above chloroformate, a fragrant, limpid liquid, b. p. 110°/14 mm., d_4^{18} 0·9136, n_D^{20} 1·4175; *di*-d-β-*octyl carbonate*, b. p. 168°/13 mm., d_4^{19} 0·8828, n_D^{20} 1·4305; *tri*-l-β-*octyl orthoformate*, $(C_8H_{17}\cdot O)_3CH$, a nearly odourless liquid, b. p. 202—203°/*ca.* 1 mm., d_4^{15} 0·8592, n_D^{15} 1·4376, made by heating ethyl orthoformate with *l*-β-octanol for 30 hours at 140°±5°; *di*-d-β-*octyl sulphite*, b. p. 133—134°/1 mm., d_4^{17} 0·9264, n_D^{20} 1·4429, made by the slow addition of thionyl chloride to *d*-β-octanol in light petroleum, at −10° to −5°, with vigorous shaking. The optical rotations of the compounds are given fully in the original.

A. C.

Dependence of Rotatory Power on Chemical Constitution. XXIII. The Normal Aliphatic Ethers of *d*-γ-Nonanol. J. Kenyon and J. W. Barnes (*J. Chem. Soc.*, 1924, **125**, 1395—1400).—With the possible exception of the methyl member, the rotatory dispersions of the ethers of this series cannot be represented by a one-term Drude equation and cases of optical heterogeneity, unaccompanied by chemical heterogeneity, appear to be presented. It is pointed out that the values for $[\alpha]_{5461}^{20}$ for this series of ethers plotted against the number of carbon atoms in the growing alkyl group attached to the ethereal oxygen atom give a smooth curve with, however, a characteristic depression at the *n*-propyl member and a similar, but much smaller, depression at the *n*-octyl member, where the group contains five more carbon atoms. A number of active ethers were prepared by treating the potassium compound of *d*-γ-nonanol in dry ether with the requisite alkyl halide. After freeing the product from uncombined *d*-γ-nonanol by heating with excess of phthalic anhydride, the ether was redistilled until its rotatory power and refractive index were constant. The following individuals are described: *methyl ether*, b. p. 74°/15 mm., n_D^{20} 1·4154, d_4^{23} 0·7926; *ethyl ether*, b. p. 88°/21 mm., n_D^{20} 1·4164, d_4^{22} 0·7901; n-*propyl ether*, b. p. 103°/23 mm., n_D^{20} 1·4193, d_4^{21} 0·7961; n-*butyl ether*, b. p. 114°/19 mm., n_D^{20} 1·4226, d_4^{21} 0·7978; n-*amyl ether*, b. p. 123°/15 mm., n_D^{20} 1·4257, d_4^{21} 0·8017; n-*hexyl ether*, b. p. 138°/17 mm., n_D^{20} 1·4283, d_4^{22} 0·8048; n-*heptyl ether*, b. p. 155°/18 mm., n_D^{20} 1·4310, d_4^{17} 0·8101; n-*octyl ether*, b. p. 166°/17 mm., n_D^{20} 1·4335, d_4^{24} 0·8085; n-*nonyl ether*, b. p. 176°/17 mm., n_D^{20} 1·4356, d_4^{24} 0·8082. For all the ethers, values for the densities over a range of temperatures are given, also a range of rotation values for different wave-lengths and temperatures. A table of the rotatory powers of the ethers in (*a*) carbon disulphide and (*b*) ethyl alcohol at room temperature, is given.

A. C.

Conductivity of some Compounds of Platinum with Thioethers. VIII. L. Tschugaev and W. Malzschewsky [compiled by E. Fritzmann] (*Z. anorg. Chem.*, 1924, **135**, 385—391).—The electrolytic conductivities of the α and β forms of the compound $PtCl_2,2Et_2S$ have been determined in solution in dry methyl and ethyl alcohols and in aqueous ethyl alcohol, the experiments being carried out at a dilution of 1 g.-mol. in 300 litres. In all cases, the molecular conductivity of the β form was the greater. In dry alcohols, the conductivities of both forms are slight, indicating that the halogen is present in a co-ordination complex. The molecular conductivity of the α variety increases greatly if the solutions are kept for some time, whilst in the case of the β variety the conductivity decreases very slightly on keeping. In aqueous alcoholic solutions, the conductivities are higher owing to slight hydrolysis. The experiments in general confirm the results of Klason (A., 1895, i, 488). When increasing quantities of thioether are added to a solution of either the α or β compound in dry methyl alcohol, the molecular conductivity increases rapidly to a limiting value of about 74. This is regarded as due to a change from a non-conducting complex compound, $[Pt,2Et_2S,Cl_2]$, to a conducting form, $[Pt,4Et_2S]Cl_2$. The sulphate compound, $PtSO_4,2Et_2S$, resembles the α chloride when in solution in dry alcohols, but is readily soluble in water with a great increase in molecular conductivity.

W. H.-R.

Conductivity of Platinum Monosulphide Compounds in Solution in Methyl Alcohol. IX. L. TSCHUGAEV and N. WLADIMIROFF [compiled by E. FRITZMANN] (*Z. anorg. Chem.*, 1924, **135**, 392—400).—The electrolytic conductivities of the α and β forms of the compound $PtCl_2,2Et_2S$, and of the corresponding propyl compound, have been determined in solution in dry methyl alcohol at a dilution of 1 g.-mol. in 500 litres. The results confirm those obtained previously for the ethyl compound at a dilution of 300 litres (cf. preceding abstract). The experiments in solution in methyl alcohol furnish a proof of the co-ordination theory in a case where hydrolysis cannot occur. The sulphide complexes are analogous to the corresponding ammonia complexes; a new series of complex compounds exists of the general form $[Pt4S]X_2$, where *S* is a monosulphide compound and X a halogen, nitrite, or nitrate ion. These are unstable in the case of monosulphide compounds, but are stable in the case of the corresponding disulphide compounds prepared from dithioethers; these compounds are strictly analogous to the diammine compounds. W. H.-R.

Electrical Conductivity of Complex Compounds of Platinum and Palladium with Organic Monoselenides. III. E. FRITZMANN (*Z. anorg. Chem.*, 1924, **133**, 133—152).—The molecular electrical conductivity of various platinum and palladium halide complexes with monoalkyl selenides in methyl alcohol solution at 25° is measured, and the effects of different halogens, concentration, the presence of an excess of alkyl selenide, and time on the conductivity are fully worked out and explained. Compounds of the types $PtX_2,2R_2S$ and $PdX_2,2R_2S$ show very slight electrical conductivity, that of the chlorine compound being the greatest and of the iodine complex the smallest. With the compound $PtCl_2,2Et_2S$, increasing dilution causes a very slight increase in μ for the α-compound, but with the β form, μ rapidly increases. The addition of increasing quantities of alkyl selenide to the solution causes, in the case of the β compound, a rapid increase in μ to a constant value, showing that ionisation has occurred by the formation of the higher type of compound $PtCl_2,4Et_2Se$, due to the passage of two chlorine atoms from the inner co-ordination sphere to the outer. Since μ has a much smaller value than that for the ternary electrolyte thus formed (236), the equilibrium $PtCl_2,4Et_2Se \rightleftharpoons PtCl_2,2R_2Se+R_2Se$ must exist in solution. With the α compound, the rate of increase in μ is much smaller, and is incomplete at the proportion of 8 mols. of added alkyl selenide, owing to the greater stability and consequent smaller lability of the *cis* modification (α) compared with the *trans* (β). In the presence of alkyl selenide, the value of μ for the α compound increases rapidly during the first half hour to a definite constant value (for each concentration), whilst for the β compound, μ decreases at the same rate to the same constant value, showing that equilibrium between the two isomerides exists in solution. Since similar constant values are not attained in the absence of alkyl selenide, equilibrium must be established by solvation with the excess of alkyl selenide. The bromine and iodine compounds of platinum and all the palladium complexes show a very slight conductivity which is practically unaffected by varying conditions, since these compounds have the *cis* configuration and hence show no characteristic phenomena of dissociation and no tendency to isomerism. The results are generally analogous to those obtained for the corresponding sulphur compounds (preceding abstracts), but with important differences in detail, due to the greater mobility of the selenium atom compared with the sulphur atom.

J. W. B.

Complex Compounds of Palladium with Organic Selenides. II. E. FRITZMANN (*Z. anorg. Chem.*, 1924, **133**, 119—132; cf. A., 1912, i, 71).—The greater mobility of the selenium atom compared with the sulphur atom prevents the existence of isomerism and causes the complexes to be less stable than the corresponding sulphur compounds. Compounds of the types $PdX_2,2R_2Se$ and $PdX_2,R{\cdot}Se{\cdot}[CH_2]_n{\cdot}Se{\cdot}R$ are produced by methods similar to those employed in the preparation of the corresponding bivalent platinum compounds (*loc. cit.*), which, in reactions, they resemble, but are monomeric and show no isomerism. They are less stable than the corresponding palladium–sulphur and platinum–selenium complexes, and the stability of the compounds formed with palladium chloride, bromide, and iodide decreases in this order.

Methyl selenium palladium chloride, $PdCl_2,2Me_2Se$, orange-red crystals, has m. p. 127—128°. Ethyl selenide forms the *compound* $PdCl_2,2Et_2Se$, orange-red crystals, m. p. 45°; *n*-propyl selenide the *compound* $PdCl_2,2Pr_2Se$, m. p. 62—62·5°; *iso*butyl selenide the *compound* $PdCl_2,2Bu_2Se$, orange-red crystals, m. p. 79°; *iso*amyl selenide the *compound* $PdCl_2,2(C_5H_{11})_2Se$, m. p. 76°, and phenyl selenide yields the *compound* $PdCl_2,2Ph_2Se$, orange-red needle clusters, m. p. 181—182°. Diethyltrimethylene diselenide yields the *compound* $PdCl_2,EtSe[CH_2]_3SeEt$, softening at 181° (decomp.). The corresponding bromine derivatives, obtained by an analogous method or by the action of excess of potassium bromide on the chlorine derivatives in alcoholic solution, are similar to the chlorine compounds, but are slightly darker in colour and form good crystals; *compound* $PdBr_2,2Me_2Se$, m. p. 129°; *compound* $PdBr_2,2Et_2Se$, m. p. 167°; *compound* $PdBr_2,2Pr_2Se$, m. p. 165°; *compound* $PdBr_2,2Bu_2Se$, m. p. 17°; *compound* $PdBr_2,2(C_5H_{11})_2Se$, m. p. 04° (?); *compound* $PdBr_2,2Ph_2Se$, m. p. 197°; *compound* $PdBr_2,EtSe[CH_2]_3SeEt$, m. p. 162°. The corresponding iodine compounds are nearly black, and are very slightly soluble in organic solvents; *compound* $PdI_2,2Me_2Se$, m. p. 123·5°; *compound* $PdI_2,2Et_2Se$, m. p. 60°; *compound* $PdI_2,2Pr_2Se$, m. p. 74°; *compound* $PdI_2,2Bu_2Se$, m. p. 147°; *compound* $PdI_2,2(C_5H_{11})_2Se$, m. p. 121°.

Gold also forms complexes with alkyl selenides which cannot be obtained except in solution, whereas the corresponding sulphur compound is stable. The corresponding bismuth complexes are prepared from potassium bismuth iodide, $BiI_3,3KI$, and are raspberry-red in colour, are much more stable than the gold compounds, and can be obtained in the solid state.

Benzyl telluride forms the *compound* $PtCl_2,2(C_7H_7)_2Te$, an orange powder which decomposes in solution with the separation of tellurium, platinum, and dibenzyl, but by rapid crystallisation from chloroform is obtained as a microcrystalline shimmering powder of greenish-gold colour which darkens and softens at 115—120°. J. W. B.

Alcoholysis. V. Alcoholysis of Esters of αβ-Unsaturated Acids and of the Corresponding Saturated Esters. B. DASANNACHARYA (*J. Indian Inst. Sci.*, 1924, **7**, 1—28).—The rates of alcoholysis of menthyl butyrate, crotonate, hydrocinnamate, and cinnamate with methyl alcohol, and of methyl butyrate, methyl crotonate, and ethyl butyrate with menthol, respectively, were measured at 30°, using excess of the alcohol in each case, and dry hydrogen chloride (0·2238—1·050*N*) as catalyst, by observing the rate of change of the optical rotation of the reaction mixture. An αβ-olefinic linking in the acyl group of an ester exerts a strong retarding influence on the alcoholysis of the ester, the mean ratio, in the cases examined, of the alcoholysis constant of the saturated to that of the unsaturated compound being 14·2. The retardation effect is less marked with menthol and menthyl esters than when methyl or ethyl alcohols and esters are alone involved. Replacement of a β-methyl group by phenyl increases the retardation, the influence of the β-group being more pronounced in the unsaturated compounds. The ratio of the constants for the direct and reverse reaction is independent of the nature of the acids (cf. A., 1921, i, 667). F. G. W.

Movement in an Electrical Field. Migration, Electrophoresis, and Electro-osmose of Sodium Oleate. M. E. LAING (*J. Physical Chem.*, 1924, **28**, 673—705).—The following general formula (in which the conductivities of the free outer ions of the "double layer" are taken into account): $n \times$(total conductivity of all constituents of a system)=(effective conductivity of any one constituent), where n is the transport number of the selected constituent, is shown to hold for all the three cases in which transport of matter accompanies conduction of electricity. Velocity of cataphoresis is not identical with mobility except when there is one electric charge per chemical equivalent. From this point of view, the only distinction between colloids and crystalloids lies in the number of chemical equivalents per unit charge.

Transport number experiments show that the movement of the various constituents of the soap (sodium oleate) system relative to the solvent is the same for the sol and gel, and in the case of gels and curds is independent of whether the solvent moves through the particles of the latter or *vice versâ*. In concentrated solutions, rather more sodium is moved towards the anode than the cathode; in a curd, this is greatly accentuated. This change with concentration is attributed to hydration, the extent of which, assuming the ionic micelle to contain very little soap, is calculated to be 10 mols. of water per equivalent of total soap. This assumption is justified, since it enables the migration data for oleate and laurate of potassium (cf. T., 1923, **123**, 2417) to be quantitatively predicted; these salts are hydrated to the extent of 13 and 17 (max.) mols. of water, respectively. The migration data for curds are predicted from a knowledge of the concentration of the mother-liquor surrounding the curd fibres.

Neither hydration nor frictional drag of the individual ion suffices to explain electro-osmosis.

The experimental evidence shows that the colloid particles in a sol are identical in number and nature with those in a gel.

S. K. T.

Tautomerism of the Mesoxalic Acid and Pyruvic Acid Phenylhydrazones. Evidence for the Hydrazone Structure of the Tautomerides. R. H. STEVENS and F. W. WARD (*J. Chem. Soc.*, 1924, **125**, 1324—1329; cf. Pechmann, A., 1893, i, 82; Dimroth, A., 1909, i, 66).—Comparison of the absorption curves of the phenyl- and phenylmethyl-hydrazones of mesoxalamide and pyruvic acid, and the phenylhydrazone of mesoxalic acid with those of azobenzene, benzeneazoformamide, benzeneazoethane, and the phenyl- and phenylmethyl-hydrazones of benzaldehyde and acetaldehyde indicates that the phenylhydrazones of mesoxalic and pyruvic acids are in truth phenylhydrazones. The following compounds are described incidentally: *Acetaldehydephenylmethylhydrazone*, a colourless oil, b. p. 136°/25 mm. The *additive product*, $NHPh{\cdot}NH{\cdot}CHMe{\cdot}CH(CO_2Et)_2,HCl$, m. p. 130°, formed by the interaction of ethylidenemalonic ester and phenylhydrazine. s-*Trichlorophenylhydrazones* of ethyl mesoxalate and of mesoxalic acid, m. p. 75° and 170°, respectively. *Bromomethylmalonamide*, white solid, m. p. 172°. *Bromoethylmalonamide*, m. p. 161·5°.

A. C.

Keto-enol Equilibrium of Ethyl Acetoacetate. Accelerators and Stabilisers. G. Rumeau (*Bull. Soc. chim.*, 1924, [iv], **35**, 762—771).—The velocity with which a specimen of ethyl acetoacetate rich in the enolic form (up to 85%) reverts to the equilibrium proportion (7% enol) at 20° is greatly influenced by the presence of other substances. Alkalis such as potassium hydroxide, sodium ethoxide, and ammonia, produce the largest increase in the velocity with which equilibrium is attained, but traces of bromine, either alone or in solution, and mineral acids are also powerful accelerators. Organic acids, such as acetic and chloroacetic acids, ferric chloride, carbon dioxide, borax, and some phenols (resorcinol, *m*-cresol), produce a smaller accelerating effect. Iodine, neutral salts, and many organic substances, including benzoic and phthalic acids, have no influence on the rapidity with which equilibrium is attained, whilst other substances, such as (in decreasing order of importance) ethyl oxalacetate, methyl *p*-hydroxybenzenesulphonate and *p*-methoxybenzenesulphonate, *p*-benzoquinone, oxalic acid, pyrocatechol, methyl salicylate, and *iso*phthalic acid decrease the velocity and act as stabilisers. With oxalacetic ester, a sample of ethyl acetoacetate kept for 4 days at 25° without special precautions was found to contain 60% of the enolic form. Solvents generally exert little influence, but benzene and carbon disulphide are weak stabilisers. Iodine bromide is a much weaker accelerator than bromine, but attempts to substitute this reagent for bromine in K. Meyer's method of determining the enolic form gave unsatisfactory results. With ethyl oxalacetate containing more than the equilibrium proportion of the keto-form, traces of bromine, potassium hydroxide, and hydrochloric acid act as accelerators, and equilibrium is at once established. R. B.

Photochemical Decomposition of Oxalic Acid in the Presence of Uranium Salts. W. C. Holmes (*Amer. Dyestuff Rep.*, 1924, **13**, 188, 197—198; cf. Freer and Gibbs, *Eighth Int. Cong. Appl. Chem.*, 1912, **20**, 153; A., 1913, ii, 88).—The photochemical decomposition of oxalic acid in the presence of uranium salts is quantitative, and might be employed in determining the light-fastness of dyes. Chemical Abstracts.

Action between Bromine and Malonic Acid in Aqueous Solution. R. W. West (*J. Chem. Soc.*, 1924, **125**, 1277—1282).—Colorimetric investigation of the action of bromine on malonic acid suggests that the change consists in (i) the unimolecular formation of bromomalonic acid and (ii) the bimolecular production of dibromomalonic acid. The unimolecular nature of the first stage indicates that the measured velocity is the slow transformation of the keto into the enolic form of the acid, and that the subsequent bromination is very rapid. The mechanism of the second stage cannot be deduced with certainty. A. C.

Rotatory Dispersion of Tartaric Acid. W. T. Astbury (*Nature*, 1924, **114**, 122).—The results of Longchambon (this vol., ii, 373) support the conclusion (A., 1923, i, 178) that the lævorotatory component in solution is substantially the same system as that which produces the strong lævorotation in the crystalline form. It follows (cf. Lowry and Austin, following abstract) that in infinitely dilute solutions the rotatory dispersion will still be anomalous, and that the dispersion in the crystal is also probably not truly normal. A. A. E.

Anomalous Rotatory Dispersion of Tartaric Acid. T. M. LOWRY and P. C. AUSTIN (*Compt. rend.*, 1924, **178**, 1902—1904).—The authors accept the theory revived by Longchambon (this vol., ii, 373) that the anomalous rotatory dispersion of tartaric acid is due to the presence of two forms in equilibrium, one lævo- and the other dextro-rotatory. Whilst the lævorotatory constituent can be obtained in crystalline form, the dextrorotatory acid can only be isolated as a derivative, and not by great dilution of the solution, as has been suggested. S. B.

Tartrates. K. P. CHATTERJEE (*J. Proc. Asiatic Soc. Bengal*, 1922, **18**, 77).—The accepted molecular volume of water of crystallisation is confirmed by observations on the following anhydrous and hydrated tartrates: *cobalt* ($2\cdot5H_2O$), *magnesium* ($2\cdot5H_2O$), *manganese* ($2H_2O$), *strontium* (H_2O), and the *salt*

$$2Cu(C_4H_4O_6),K_2(C_4H_4O_6),3H_2O.$$

CHEMICAL ABSTRACTS.

Walden Inversion. P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1924, **59**, 473—478).—A change in the sign of the rotation of the compounds is observed when β-thioloctane is oxidised to the corresponding sulphonic acid. In this instance, the change of the polarity of one group brought about without substitution results in a change of the direction of rotation. D. R. N.

Walden Inversion. II. The Optical Rotation of α-Thiolpropionic and Corresponding α-Sulphopropionic Acids. P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1924, **60**, 1—3).—In a previous communication (preceding abstract) it was suggested that the oxidation of thiol derivatives, in which the radicals attached to the asymmetric carbon atom were of a different polarity from the corresponding sulphonic acid derivatives, might leave the direction of rotation unchanged. This has been confirmed. *d*-Thiolpropionic acid was oxidised to α-sulphopropionic acid, which rotated in the same direction as the parent substance. C. T. G.

Absorption of Ultra-violet Rays by Acraldehyde. V. HENRI.—(See ii, 513.)

Compounds of Magnesium Alkyl Halides with Carbonyl Compounds and the Reducing Action of Grignard Reagents. K. HESS and W. WUSTROW.—(See i, 859.)

Production of Acetone from Acetates and Acetic Acid. M. G. KEKRE, J. J. SUDBOROUGH, and H. E. WATSON (*J. Proc. Asiatic Soc. Bengal*, 1922, **18**, 77).—By distillation, barium acetate yields more acetone than calcium or magnesium acetate. Yields of 80—90% are obtained in the continuous production of acetone from acetic acid, using magnesium, calcium, and barium acetates and pumice as catalysts. CHEMICAL ABSTRACTS.

Some New Pinacolines. R. LOCQUIN and L. LEERS (*Compt. rend.*, 1924, **179**, 55—57).—The dehydration of trimethyl*iso*propylglycol yields: (1) mainly βγγ-*trimethylpentan*-δ-*one*,

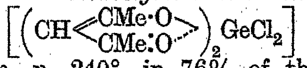
$$CHMe_2·CMe_2·CO·CH_3,$$

b. p. 150—151°/750 mm., d_4^0 0·856, which forms a *semicarbazone*, m. p. 150°, and an *oxime*, b. p. 104—105°/14 mm., m. p. 41°, and (2) a small proportion of the isomeric ββδ-trimethylpentan-γ-one (cf. Nef, A., 1900, i, 349; Haller and Bauer, A., 1909, i, 108; 1913, i, 829). Dehydration of trimethyl*iso*butylglycol gives only βδδ-*trimethylhexan*-ε-*one*, $CHMe_2·CH_2·CMe_2·CO·CH_3$, b. p. 164—165°/750 mm., d_4^0 0·845, which forms a *semicarbazone*, m. p. 133°, and an *oxime*, b. p. 110—111°/14 mm., m. p. 61°, and is isomeric with ββε-trimethylhexan-γ-one (cf. Haller and Bauer, *loc. cit.*).

From these results and those previously published, it follows that dehydration of pinacones of the form $OH·CMeR·CMe_2·OH$, where R represents ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *iso*propyl, *iso*butyl, or *tert.*-amyl, yields in preponderating proportion the pinacoline $CMe_2R·CO·CH_3$. With trimethyl*iso*propylglycol and still more so with the higher glycols, small proportions of the isomeric pinacolines are also formed.

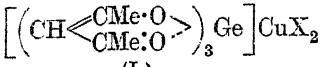
Pinacolines containing the group $CO·CH_3$ may be obtained perfectly pure by means of their oximes or semicarbazones, which crystallise well and are readily decomposed when boiled with concentrated oxalic acid solution. T. H. P.

Researches on Residual Affinity and Co-ordination. XIX. Interactions of Germanium Tetrahalides and β-Diketones. G. T. MORGAN and H. D. K. DREW (*J. Chem. Soc.*, 1924, **125**, 1261—1269).—With the exception of germanium, the members of both families of the fourth vertical series of the periodic classification have yielded characteristic compounds with acetylacetone and other β-diketones. Germanium tetrachloride was found to react energetically with acetylacetone in anhydrous solvents (chloroform) forming *germanium bisacetylacetone dichloride*,



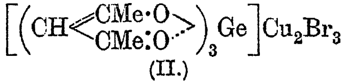
$$\left[\left(CH{<}{\begin{matrix}CMe·O\\CMe:O\end{matrix}}{>}\right)_2GeCl_2\right]$$

colourless prisms, m. p. 240°, in 76% of the theoretical yield. *Germanium bisacetylacetone dibromide*, a colourless, microcrystalline powder, m. p. 226° (intumescence), and *germanium bispropionylacetone dichloride*, a white, crystalline powder, m. p. 128—129°, are also described. Germanium tetrachloride, allowed to interact with copper acetylacetone in cold chloroform solution for 24 hours, formed an insoluble greenish-white additive product which yielded an olive-brown solution when boiled with acetylacetone and left a residue of cuprous chloride. On cooling, the solution deposited successively (i) colourless germanium bisacetylacetone dichloride; (ii) dark blue *needles*, $Ge_2(C_5H_7O_2)_6Cl_7Cu_3$, m. p. (generally) 137—139°. When the latter was treated with cold chloroform, copper chlorides were deposited and the solution yielded colourless *germanium trisacetylacetone cuprochloride* (I), m. p. 147—148°;



$$\left[\left(CH<\begin{matrix}CMe\cdot O\\CMe:O\end{matrix}>\right)_3Ge\right]CuX_2$$

(I.)



$$\left[\left(CH<\begin{matrix}CMe\cdot O\\CMe:O\end{matrix}>\right)_3Ge\right]Cu_2Br_3$$

(II.)

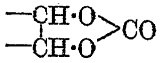
(iii) a green powder decomposed by aqueous chloroform into cupric chloride and copper acetylacetone; (iv) transparent orange to yellow crystals, $(C_5H_7O_2)_7Cl_5Cu_2Ge_2$, m. p. 128—129°; (v) colourless prisms, m. p. 147—148° (I) above. Germanium tetrabromide (3 mols.) reacts with copper acetylacetone in chloroform to form a blue solution and a dark precipitate which yielded cuprous bromide and a small quantity of germanium trisacetylacetone dicuprobromide on treatment with boiling acetylacetone; the blue solution gave bromoacetylacetone and a mixture of germanium trisacetylacetone cupri- and dicupri-bromides from which *germanium trisacetylacetone cuprobromide,* m. p. 165—166°, was isolated by addition of copper acetylacetone dissolved in chloroform. *Germanium trisacetylacetone dicuprobromide* (II), m. p. 195°, and *germanium trisacetylacetone cupribromide,* $C_{15}H_{21}O_6Br_3CuGe$, m. p. 139°, are also described. A. C.

Light Absorption of the Pigment formed in the Orcinol Reaction for Pentoses. G. SCHEFF (*Biochem. Z.*, 1924, **147**, 90—93).—A comparison of the absorption spectrum of an amyl-alcoholic solution of the blue pigment formed on applying the orcinol reaction to arabinose and xylose with the data previously obtained by Bergell and Pschorr (*Z. physiol. Chem.*, 1903, **38**, 16) in a less accurate form. J. P.

Thermal Fractionation of Gaseous Products from the Pyrogenic Decomposition of certain Definite Compounds. P. LEBEAU (*Compt. rend.*, 1924, **178**, 2256—2259).—Curves are plotted showing the volume of gas evolved at various temperatures up to 1000° during the pyrogenic decomposition of various non-volatile organic compounds (*e.g.*, starch, casein, dextrose, sucrose). The form of the curves is related to the constitution of the substance carbonised, *e.g.*, the curves for sucrose and dextrose show a close similarity. The method may thus afford information as to the constitution of organic compounds of high molecular weight. W. T. K. B.

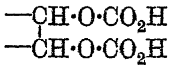
Optical Inactivity of Active Sugars in the Adsorbed State. I. S. S. BHATNAGAR and D. L. SHRIVASTAVA (*J. Physical Chem.*, 1924, **28**, 730—743).—The rotatory powers of optically active sugars in presence of adsorbing colloids (*e.g.*, arsenic and antimony sulphides) are always less than those calculated from Beer's law; the discrepancy decreases with increasing dilution and increases with increasing excess of sol over sugar. The sugar adsorbed by the colloid loses its optical activity, which supports the chemical affinity theory of protective action. S. K. T.

Sugar Carbonates and their Derivatives. I. C. F. ALLPRESS and W. N. HAWORTH (*J. Chem. Soc.*, 1924, **125**, 1223—1233).—Sugar carbonates corresponding with normal (A) and acid carbonates (B) have been prepared by acting on the sugars with chloroformic esters in the presence of (i) sodium hydroxide or (ii) pyridine.



$$\left.\begin{matrix}-CH\cdot O\\ -CH\cdot O\end{matrix}\right>CO$$

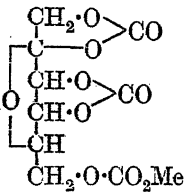
(A)



$$\begin{matrix}-CH\cdot O\cdot CO_2H\\ -CH\cdot O\cdot CO_2H\end{matrix}$$

(B)

The normal carbonates of the sugars resemble the acetone sugar derivatives in their tendency to crystallise and ease of hydrolysis with dilute acids, but the carbonates are readily hydrolysed to the free sugars on gentle warming with dilute alkalis.



(I.)

Monocarbomethoxyfructose dicarbonate (I), prepared by method (i), has m. p. 192°, $[\alpha]_D$ −78·5° in acetone (c=0·82) and −72·2° in ethyl acetate (c=0·24). The alcohol washings from (I) deposited needles of a strongly lævorotatory difructose *derivative*, $C_{17}H_{18}O_{16}$, m. p. 196°. *Tetracarbomethoxyfructose*, prisms, m. p. 126—127°, resulted from the condensation of fructose in chloroform with dry pyridine and methyl chloroformate (method ii), $[\alpha]_D$ −75·1° (c=2·47), −77·6° (c=2·04) in acetone and −98·1° (c=1·44) in chloroform. On keeping the solutions, in sunlight or in the dark at a constant temperature, anomalous variations in the rotation values were observed. *Tetracarbethoxyfructose*, also by method (ii), formed crystals, m. p. 118°, $[\alpha]_D$ −97·0° to 95·3° in chloroform (c=1·6), and −72° in acetone (c=0·6); an *isomeride*, a yellow syrup, $[\alpha]_D$ −19° in acetone (c=2·4), accompanied the last compound. Galactose by method (i) gave rise to *tricarbomethoxygalactose carbonate*, needles, m. p. 170·5—171°, $[\alpha]_D$ −88·9° in acetone (c=0·53). The later deposits contained an *isomeride*, a colourless, amorphous powder, m. p. 126°, $[\alpha]_D$ from −29·8° to −45° in acetone (c=0·40), and −34·9° in chloroform (c=1·1); the rotations showed variations according as the solutions were kept in the light or in the dark. With pyridine as condensing medium, the reaction proceeded with extreme difficulty. *Tetracarbomethoxygalactose* with $[\alpha]_D$ +92·6° in acetone (c=1·86), was obtained as a yellow glass, accompanied by much unaltered galactose. Dextrose by method (i) yielded *tetracarbomethoxyglucose*, an amber-coloured glass having $[\alpha]_D$ +34·6° (c=1·56) and +34·1° (c=0·73) in ethyl alcohol, $[\alpha]_D$ +34·8° (c=0·52) and +51·3° (c=2·2) in acetone. On methylating with Purdie's reagent, vitreous *tetracarbomethoxymethylglucose* was obtained. Using method (ii) a *tetracarbomethoxyglucose*, $[\alpha]_D$ +87·1° (in acetone), different from the above, was obtained. Mannitol [method (i)] yielded *dicarbomethoxymannitol dicarbonate*, a yellow gum, $[\alpha]_D$+29·6° in acetone (c=1·2). Sucrose reacted with difficulty in pyridine and yielded a hepta (or octa) *carbomethoxy* derivative, $[\alpha]_D$ +53·8° in acetone (c=1·0), as a pale yellow glass. This product showed unexpected stability towards 1% hydrochloric acid at 100°.

A. C.

Structure of Diacetone [Di*iso*propylidene] Glucose. II. γ-Methylglucuronic Acid and δ-Methylglucoheptonolactone. P. A. Levene and G. M. Meyer (*J. Biol. Chem.*, 1924, **60**, 173—178).—On reduction of the monomethylsaccharolactone, obtained by oxidation of monomethylglucose, *d*- (and not *l*-)γ-methylglucuronic acid is formed. This indicates that the methyl group in monomethylglucose is in the γ position. The position of the new substance in the *d*-series was shown by the properties of the *p*-bromophenylhydrazine derivative, which has the same character of mutarotation as the corresponding derivative of glucuronic acid, *i.e.*, a decrease in numerical value and direction to the left. It is further shown that the methylglucoheptonolactone obtained from the methylglucose was dextrorotatory, which agrees with the γ-position for the methyl group; δ-methylglucose should give a lævorotatory heptonolactone.

d-γ-Methyl-α-glucoheptonolactone was also prepared by the action of hydrocyanic acid on methylglucose and was found to form a γ-methyl sugar acid. C. T. G.

Derivatives of a New Form of Mannose. J. C. Irvine and W. Burt (*J. Chem. Soc.*, 1924, **125**, 1343—1348).—Conditions are given for the preparation of a mixture of two new mannosides which displays properties similar to Fischer's γ-methylglucoside. The name "γ-methylmannoside," as used here, refers to a preparation containing two stereoisomeric forms of the compound which differ from each other in the position of the methyl group and from α-methylmannoside in the linking of the internal ring.

γ-*Methylmannoside* is a very viscous syrup, $[\alpha]_D^{20}$ +80·2° in ethyl alcohol, which immediately reduces neutral permanganate. It is converted successively by means of silver oxide and methyl iodide into mixtures of *trimethyl-γ-mannosides* and *tetramethyl-γ-mannosides*, b. p. 141°/13 mm., n_D 1·4482, $[\alpha]_D^{20}$ +24·9° in ethyl alcohol. The tetramethyl derivatives are hydrolysed to *tetramethyl-γ-mannose*, a crystalline solid, b. p. 190°/10 mm., n_D 1·4647, $[\alpha]_D^{20}$ +47·4° in ethyl alcohol. During methylation, particularly by the methyl sulphate method, a partial conversion of γ- into α-forms occurs. In preparing γ-methylmannoside by the method involving concentrated hydrochloric acid, auto-condensation of γ-mannose derivatives appears sometimes to take place. A. C.

Two Isomeric Tetramethylmannonolactones. P. A. Levene and G. M. Meyer (*J. Biol. Chem.*, 1924, **60**, 167—171).—The α- and β-isomerides in sugars with different oxidic structures may be determined by the position of the hydroxyls with respect to the oxidic ring. In mannose, both the butylene and amylene oxide rings have the same direction and possibly some of the abnormalities in the behaviour of mannose may be due to a peculiarity in the oxidic ring, although it is also possible that in solution the two oxidic forms reach an equilibrium. In view of these considerations, the lactones obtained by oxidation of tetramethylmannose and by methylation of mannonolactone were compared. The former, prepared by oxidation of tetramethylmannose with bromine, is a liquid and is dextrorotatory ($[\alpha]_D^{20}$ +105°) as are also the free acid ($[\alpha]_D$ +17·5°) and its sodium salt ($[\alpha]_D$ +41·6°). The latter, prepared by methylation of mannonolactone by Purdie's method, is crystalline, m. p. 107°; it is dextrorotatory ($[\alpha]_D$, in water, +65·2°), whilst the free acid, $[\alpha]_D$ −25·3°, and its sodium salt, $[\alpha]_D$ −22·5°, are lævorotatory. The rotation of the two tetramethyl-lactones in opposite directions requires elucidation. C. T. G.

Relation between Hexosemonophosphoric Acid and Hexosediphosphoric Acid. C. Neuberg and E. Reinfurth (*Biochem. Z.*, 1924, **146**, 589—593).—The acid phenylhydrazine salt of hexosemonophosphoric acid osazone is identical with that prepared from hexosediphosphoric acid by the elimination of one phosphoric acid residue. It is concluded that by subjecting hexosediphosphoric acid to gentle hydrolysis the α-phosphoric acid residue is removed. J. P.

Action of Ultra-violet Light on Lævulose. Production of Carbon Monoxide and Formaldehyde. H. Bierry and A. Ranc (*Bull. Soc. chim.*, 1924, [iv], **35**, 771—772).—The decomposition of lævulose by ultra-violet light, yielding carbon monoxide, carbon dioxide, and formaldehyde, described by D. Berthelot (this vol., ii, 320), has been previously observed by the authors (A., 1910, i, 652). The decomposition takes place at 10—20°, more rapidly at 60—70°. R. B.

Posidonia Fibre. II. The Cellulose. J. C. Earl (*J. Chem. Soc.*, 1924, **125**, 1322—1323; cf. T., 1923, **123**, 3223).—The cellulose of *Posidonia australis* is converted by Irvine and Hirst's method (T., 1922, **121**, 1585) into the *tri-acetate*, $[\alpha]_D$ −39·8° in chloroform, which is converted by methyl-alcoholic hydrogen chloride to the extent of 95% into a mixture of α- and β-methylglucosides. Posidonia, like cotton, cellulose appears to belong to the polyanhydroglucose type, but the great difference in optical rotation of the triacetates of the celluloses indicates a difference in their chemical structure. A. C.

Preparation of Acetone-soluble Cellulose Acetate. G. Kita, K. Asami, J. Kato, and R. Tomihisa (*Z. angew. Chem.*, 1924, **37**, 414—418).—Dry cellulose (cotton paper) is added to a mixture of glacial acetic acid, acetic anhydride, and a little sulphuric acid cooled with ice water. The mixture is then transferred to a thermostat and the reaction temperature carefully controlled. Hydration is effected by a mixture of equal weights of glacial acetic acid and water. If the hydration temperature is too high, the viscosity of the product does not increase and the copper value increases with the time of hydration, whilst the reverse is the case with a suitably low temperature. The influence of temperature is more marked during acetylation than during hydration. Acetylation at a relatively high temperature (*e.g.*, 25°) gives an inferior acetone-soluble acetate even if hydration is effected at a low temperature, whilst the temperature of hydration has comparatively little influence with a product of low-temperature acetylation.

The most suitable temperature depends on the quantity of sulphuric acid added as catalyst, a smaller quantity of the latter being required at higher temperatures, although with too small a quantity a good acetate is unobtainable. If the quantity of catalyst and the time of acetylation are suitably limited, good results may be obtained even at higher temperatures. There is no advantage in neutralising the sulphuric acid on hydration. W. T. K. B.

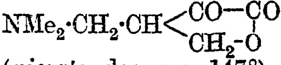
Gelatinisation by Heat of Wheat and Maize Starch. C. L. ALSBERG and O. S. RASK (*Cereal Chem.*, 1924, **1**, 107—116).—Suspensions of wheat and maize starch, on slow heating, showed constant viscosities up to about 65° and then steady increases in viscosity to maxima at 91° for maize starch and 95° for wheat starch. Gelatinisation does not take place at a sharply defined transition point, but is a long and gradual process, which does not necessarily commence at the so-called gelatinisation temperature. The disappearance of anisotropy marks an early stage in the gelatinisation process, but not its completion. E. M. C.

Lignin Hydrochloride. E. HÄGGLUND and C. B. BJÖRKMAN (*Biochem. Z.*, 1924, **147**, 74—88).—The preparation is described of a lignin hydrochloride by treatment of finely-powdered pine wood with highly concentrated hydrochloric acid in the cold. The yield is 22—26% of the weight of the wood after extraction with acetone and ether. The lignin is partly dissolved by further treatment with concentrated acid in the cold, with the liberation of reducing sugars. A similar result is achieved by boiling with dilute acids, and by a combination of the hot and cold treatments more than 50% of the lignin is dissolved. The sugar formed is partly fermentable—the non-fermentable part consisting of arabinose. No methylpentose is present. The lignin hydrochloride yields an alcohol-insoluble furfuraldehyde phloroglucide indicating the presence of pentosans, and a phloroglucide soluble in alcohol which is not a methylfurfuraldehyde phloroglucide. Previous determinations of methylpentoses in lignins are therefore not trustworthy. The green colour of the solution and residue of wood treated with strong hydrochloric acid is regarded as indicative of a lignin–carbohydrate complex, since the similar colour produced by lignins freed from carbohydrate is brown, whilst the solution is violet. More trustworthy quantitative determinations of lignin are obtained by prolonged treatment with highly concentrated acid than by short treatment. Lignin hydrochloride gives rise to oxalic acid on alkali fusion, and to succinic acid on oxidation with hydrogen peroxide (cf. Holmberg, A., 1923, i, 1067; Fischer, A., 1923, i, 185). J. P.

Condensation of Ethyl Diethylammonium Malonate with Formaldehyde. C. MANNICH and K. RITSERT (*Ber.*, 1924, **57**, [*B*], 1116—1118).—The condensation of ethyl diethylammonium malonate with formaldehyde at a low temperature gives rise to a mixture of ethyl β-diethylaminopropionate and *ethyl ββ-bisdiethylaminoisobutyrate*, $CO_2Et{\cdot}CH{\cdot}[CH_2{\cdot}NEt_2]_2$, which could not be separated completely from one another by fractional distillation. The former substance is identified as the *hydrochloride*, the latter as the *chloroplatinate*, m. p. 210° (decomp.). With similar mono-alkylated derivatives of malonic acid, analogous condensation products are doubtless formed primarily which immediately decompose into esters of α-substituted acrylic acids, diethylamine, carbon dioxide, and water. Thus ethyl diethylammonium ethylmalonate and formaldehyde yield *ethyl α-ethylacrylate* [*α-methylenebutyrate*], b. p. 138°. *Ethyl α-methylacrylate*, b. p. 118°, *ethyl α-benzylacrylate*, b. p. 134°/15 mm. (*α-benzylacrylic acid*, m. p. 68°), and *ethyl α-allylacrylate*, b. p. 60°/16 mm. (*α-allylacrylic acid*, b. p. 159—161°) are prepared similarly. H. W.

Synthesis of Aminoketonic Acids. C. MANNICH and M. BAUROTH (*Ber.*, 1924, **57**, [*B*], 1108—1115).—The synthesis of ketonic bases from formaldehyde, ketones, and amine salts (cf. A., 1922, i, 351, and previous abstracts) has been extended to α-, β-, and γ-keto-acids.

The action of formaldehyde (35%) on a mixture of pyruvic acid and dimethylamine hydrochloride leads to the production of the *hydrochloride* of *α-keto-β-dimethylaminomethyl*-n-*butyrolactone*,



$NMe_2\cdot CH_2\cdot CH{<}\begin{matrix}CO-CO\\ CH_2-O\end{matrix}$, m. p. 168° (decomp.) when rapidly heated (*picrate*, decomp. 147°), which is reduced by tin and concentrated hydrochloric acid to *α-hydroxy-β-dimethylaminomethylbutyrolactone hydrochloride*, m. p. 190°. Similarly, pyruvic acid, formaldehyde, and piperidine hydrochloride yield *α-keto-β-piperidinomethyl*-n-*butyrolactone hydrochloride*, m. p. 180° (decomp.) [*picrate*, m. p. 147° (decomp.)], which is reduced to *α-hydroxy-β-piperidinomethyl*-n-*butyrolactone hydrochloride monohydrate*, m. p. 135° (decomp.) after softening at 100°. α-Ethylacetoacetic acid, formaldehyde, and dimethylamine appear to yield primarily the expected amino-acid which, however, readily evolves carbon dioxide and passes into *γ-dimethylaminomethylpentan-β-one*, $CH_3\cdot CO\cdot CHEt\cdot CH_2\cdot NMe_2$, b. p. 62—64°/14 mm.; the hygroscopic *hydrochloride*, m. p. 131°, the *picrate*, the *oxime hydrochloride*, m. p. 178° (decomp.), and the *methiodide*, m. p. 146°, are described. *γ-Piperidinomethylpentan-β-one*, prepared in a similar manner, has b. p. 108—110°/15 mm.; it yields a *hydrochloride*, m. p. 136°; *picrate*, m. p. 134°; *oxime hydrochloride*, m. p. about 200° when rapidly heated, and methiodide, m. p. 119—120°. Lævulic acid is transformed by formaldehyde and dimethylamine hydrochloride at 110° into *γ-keto-ε-dimethylaminohexoic acid hydrochloride*,

$$NMe_2\cdot[CH_2]_2\cdot CO\cdot[CH_2]_2\cdot CO_2H,HCl,$$

m. p. 119—120°; the corresponding *picrate*, m. p. 140—143°, and the *hydrochloride* of the *semicarbazone*, decomp. about 165° when rapidly heated, are described. The substance is converted by phenylhydrazine at 100° into the *phenylhydrazide* of 1-*phenylpyrazoline*-3-*propionic acid*, m. p. 150°. *γ-Keto*-1-*piperidino*-n-*hexoic acid hydrochloride* crystallises in leaflets, m. p. 145—146°, and yields a *semicarbazone hydrochloride*, decomp. about 190°; it is converted by phenylhydrazine into 1-phenylpyrazoline-3-propionphenylhydrazide and piperidine. H. W.

Influence of Acids and Alkalis on Amino-acids. E. ABDERHALDEN and E. SCHWAB (*Z. physiol. Chem.*, 1924, **136**, 219—223).—Using pure glycine, leucine, alanine, and glutamic acid, the authors were unable to confirm the results of Zelinski and Sadikov (A., 1923, i, 1185), who found that glycine loses nitrogen as ammonia under the influence of $N/10$-sodium hydroxide. It is suggested that the changes observed are due to impurities and possibly to faulty technique in the formol titration. The conversion of glutamic acid into glutimic acid by heat was confirmed.

O. O.

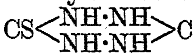
Do Creatine and Creatinine give the Diazo Reaction? H. REINWEIN (*Z. Biol.*, 1924, **81**, 49—50).—Various preparations of creatinine and creatine that gave the diazo reaction (Pauly, A., 1904, i, 1068) no longer did so when purified by repeated recrystallisation. It is suggested that the reaction before purification was due to traces of iminazole derivatives such as histidine, which is a normal constituent of mammalian muscle and might be precipitated with creatine and creatinine in their preparation from muscle and from urine. C. T. G.

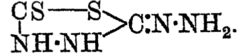
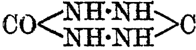
Methylethylmaleinimide. WILLIAM KÜSTER (*Z. physiol. Chem.*, 1924, **137**, 78—84; cf. A., 1901, i, 298; 1906, i, 337; 1917, i, 443).—Methylethylmaleinimide is prepared in 80% yield by boiling methylethylmaleic anhydride with alcoholic ammonia. The action of boiling aqueous potassium hydroxide solution on methylethylmaleic anhydride yields two acids, m. p. 184° (decomp.) and 126—130°, respectively. The *copper* salts have the composition $C_7H_8O_4Cu,\frac{1}{2}H_2O$. B. F.

The Equilibrium between Thiocarbamide and Ammonium Thiocyanate. G. H. BURROWS (*J. Amer. Chem. Soc.*, 1924, **46**, 1623—1627).—The equilibrium between thiocarbamide and ammonium thiocyanate has been investigated when the substances are melted together at temperatures from 132° to 182°. Side reactions occur with the formation of hydrogen sulphide and ammonia. The percentages of ammonium thiocyanate in the equilibrium mixtures were 66·5, 73·4, and 77·8 at 132°, 156°, and 182°, respectively. The equilibria in n-propyl and n-butyl alcohols varied with the nature of the solvent, whilst the temperature coefficient in the presence of these solvents was of opposite sign to that in the case of the fused mixture. These effects are ascribed to a change in equilibrium, as the specimens were chilled before analysis. The heat of transformation of 1 mol. of ammonium thiocyanate into 1 mol. of thiocarbamide is calculated to be 4600 cals.

W. H.-R.

Preparation of Thiocarbohydrazide: Mono- and Di-thio-p-urazine. P. C. GUHA and S. C. DE (*J. Chem. Soc.*, 1924, **125**, 1215—1218).—Thiocarbohydrazide was prepared in 70% yield by heating alcoholic solutions of hydrazine hydrate (2 mols.)

and diethyl xanthate under reflux. The *diacetyl* derivative had m. p. 180—181°. *Dimethylenethiocarbohydrazide*, obtained by heating thiocarbohydrazide with excess of formaldehyde, had m. p. 204—205° (decomp.). Thiocarbohydrazide and carbohydrazide react with thiocarbimides, forming bisthiocarbamyl derivatives: $XC(NH\cdot NH_2)_2+2RCNS=XC(NH\cdot NH\cdot CS\cdot NHR)_2$ ($X=S$ or O; $R=Ph$ or $p\text{-}C_7H_7$). *Thiocarbohydrazide-dicarbonthiophenylamide* has m. p. 199°. The compound for which $X=S$, $R=p\text{-}C_7H_7$, melts at 201°; $X=O$, $R=Ph$, has m. p. 208—209°; $X=O$, $R=p\text{-}C_7H_7$, m. p. 215—216°. Potassium ethyl xanthate reacts with thiocarbohydrazide in a sealed tube at 100°, giving *dithio-*p*-urazine*,  $CS<{}^{NH\cdot NH}_{NH\cdot NH}>CS$, m. p. 202—203°, which forms a *disilver* salt and a *dibenzyl ether*, m. p. 142°, but no benzylidene derivative.

Purgotti and Vigano's "dithio-*p*-urazine," m. p. 198—199° (A., 1902, i, 323), probably has the constitution  $\begin{matrix}CS\text{—}S\\ |\qquad\\ NH\cdot NH\end{matrix}>C{:}N\cdot NH_2$. *Dithio-*p*-urazine disulphide*, obtained by the action of iodine on dithio-*p*-urazine, has m. p. 218° (decomp.). *Monothio-*p*-urazine*,  $CO<{}^{NH\cdot NH}_{NH\cdot NH}>CS$, m. p. 238° (decomp.), was prepared by heating thiocarbohydrazide with carbamide at 130°, or by heating carbohydrazide with potassium ethyl xanthate in a sealed tube at 100°. p-*Urazine*, m. p. 264—265°, was obtained by heating carbohydrazide with carbamide at 120°. A. C.

Mustard Oils. L. ROSENTHALER (*Arch. Pharm.*, 1924, **262**, 126—127).—Allyl *iso*thiocyanate forms a compound with potassium hydrogen sulphite. Although *a priori* the allyl group might have as much claim to be considered the active agent as the *iso*thiocyanate group, yet the instability of the compound, among other evidence, suggests that the latter is really responsible. The compound should therefore be formulated $C_3H_5\cdot NH\cdot CS\cdot SO_2\cdot OK$.

W. A. S.

Reaction between Mercuric Cyanide and certain Metals in Liquid Ammonia. F. W. BERGSTROM (*J. Amer. Chem. Soc.*, 1924, **46**, 1559—1568).—Aluminium reacts with a solution of mercuric cyanide in liquid ammonia with the initial formation of two liquid phases, the denser of which contains one or more double cyanides of mercury and aluminium, which cannot, however, be crystallised. By further action with excess of aluminium, a solution of aluminium cyanide in liquid ammonia is formed, which shows a transition temperature between 0° and —33°. Crystals deposited at room temperature have the composition $Al(CN)_3,5NH_3$, whilst those obtained at —40° correspond with

$$Al(CN)_3,13(\text{or }14)NH_3.$$

In addition, products with $1\frac{1}{2}$(?), 6, and 9 mols. of ammonia have been obtained.

The *compound* $Hg(CN)_2,Mn(CN)_2,2\text{—}3NH_3$ is obtained by the action of manganese on a solution of mercuric cyanide in liquid ammonia. Two liquid phases are again formed, but the action then stops and manganous cyanide is not produced. Mercuric cyanide and metallic magnesium react in liquid ammonia to form two liquid phases, the denser of which disappears, leaving a grey precipitate of ammoniated magnesium cyanide. Zinc, iron, and tin also react with mercuric cyanide in liquid ammonia.

W. H.-R.

Cuprous–Cupric Cyanide Ammine Compounds. A. Benrath and W. Schröder (*Z. anorg. Chem.*, 1924, **135**, 205—225).—The conditions for the inter-transformation of compounds of the tetra- and tri-cyanogen series of copper ammines are considered. A new blue *salt*, $[Cu_2(CN)_3NH_3]_2[Cu(NH_3)_4]$, is prepared by the action of gaseous ammonia on the violet diammine,

$$[Cu_2(CN)_3NH_3]_2[Cu(NH_3)_2].$$

The compound $[Cu_2(CN)_4][Cu(NH_3)_6]$ is made from the corresponding triammine by the action of ammonia (cf. *Compt. rend.*, 1853, **36**, 1099); Malmberg (A., 1898, i, 547) and Treadwell (A., 1904, i, 479) denied its existence. Treadwell's formulæ for these compounds are adversely criticised; new ones are proposed, based on the assumption that the dark blue, easily soluble salts with the smallest ammonia content are tetrammine copper salts. The solubility curve (in ammonia solution at 10°) of the green salt, $[Cu_2(CN)_4][Cu(NH_3)_3]$, of the tetracyanogen series, is discontinuous at an ammonia concentration of 3·614 g. per 100 g. of water, and the curve thereafter represents the solubility of the blue tetrammine, $[Cu_2(CN)_4][Cu(NH_3)_4]$. It falls to a minimum and then rapidly increases, indicating the formation of a higher complex (hexammine). At 40°, the solution deposits a brown substance, or, if the ammonia content is high, the violet salt of the tricyanogen series appears. At these temperatures, the curve becomes continuous. The violet salt of the tricyanogen series, when shaken with ammonia, forms the green salt of the tetracyanogen series. At low temperatures this is reversed; the reverse reaction is slow unless the solution is "seeded" with a crystal of the green salt. In presence of small quantities of ammonia, the green salt is converted completely into the violet at 70°; cuprous cyanide must be produced first, its formation being assisted by increasing the temperature and hindered by raising the ammonia concentration. Tetrammine salts of the tricyanogen series are readily converted into members of the tetracyanogen series in presence of moisture. Previous work is criticised.

S. K. T.

Hydrolysis of Potassium Ferricyanide and Potassium Cobalticyanide by Sulphuric Acid. H. Bassett and A. S. Corbet (*J. Chem. Soc.*, 1924, **125**, 1358—1366).—Boiling sulphuric acid (80%) hydrolyses potassium ferricyanide according to the equation: $2K_3Fe(CN)_6+11H_2SO_4+13H_2O=3K_2SO_4+6(NH_4)_2SO_4+2FeSO_4+11CO+CO_2$. On progressive dilution of the acid, the reaction tends more and more towards the equation $2K_3Fe(CN)_6+6H_2SO_4=3K_2SO_4+Fe_2(SO_4)_3+12HCN$.

Potassium cobalticyanide is hydrolysed by the concentrated acid in the same way as above. Prolonged boiling, in a reflux apparatus, with 30% acid causes the reaction $2K_3Co(CN)_6+6H_2SO_4+2H_2O=3K_2SO_4+2CoSO_4+NH_4HSO_4+11HCN+CO_2$. A white, crystalline, intermediate product, probably potassium aquopentacyanocobaltate, was isolated in this case; a similar compound was obtained by the action of bromine on potassium cobalticyanide. S. K. T.

Mixed Organo-aluminium Compounds. Aluminium Mono-ethyl Di-iodide and Aluminium Diethyl Iodide. V. Grignard and R. Jenkins (*Compt. rend.*, 1924, **179**, 89—92).—Aluminium powder and ethyl iodide (dry and free from alcohol) react readily in an atmosphere of dry nitrogen to give a mixture of *aluminium diethyl iodide*, $AlEt_2I$, a clear, mobile liquid, b. p. 118—120°/4—5 mm., d_{27}^{4} 1·609, and *aluminium ethyl di-iodide*, $AlEtI_2$, a solid, m. p. 35—37°, b. p. 158—160°/4 mm. Both compounds ignite spontaneously when exposed to air; the corresponding etherates do not exhibit this property. W. T. K. B.

The Decomposition of Lead Tetra-ethyl and its Application to Explosion Motors. P. Jolibois and G. Normand (*Compt. rend.*, 1924, **179**, 27—28).—Lead tetraethyl, prepared in a pure state by the action of lead chloride on magnesium ethyl iodide, is completely decomposed at 400° with the production of finely-divided metallic lead. It is suggested that this affords an explanation of the observed action of lead tetraethyl, which, when mixed with the fuel of explosion motors, allows greater compression without the danger of self-ignition. By increasing the radius of curvature of the sharp-edged particles by the deposition thereon of the lead, the tendency to self-ignition is reduced in accordance with the observations of Reboul (A., 1913, ii, 303, 489). [Cf. *B.*, 1924, 700.] J. W. B.

Mercury Ethylmercapto-salts. G. Sachs (*Z. anorg. Chem.*, 1924, **135**, 273—282).—Mercuric ethylmercaptoacetate,

$$Et\cdot SHg\cdot OAc,$$

is obtained when mercury mercaptide is shaken with mercuric acetate solution. By precipitating an aqueous solution of the mercaptoacetate with alkali-metal salts of the appropriate acids, the corresponding chloride, bromide (which was not crystalline; cf. A., 1898, i, 458), nitrate (crystalline), *normal carbonate* (m. p. 140°), and *benzoate* are obtained. The phosphate appears to be soluble.

The benzoate melts at 130° to 140°, solidifies at 160°, and remelts at 170° (decomp.), yielding benzoic acid, ethyl benzoate, *o*-hydroxymercuribenzoic anhydride, diethyl mono- and di-sulphides, mercuric sulphide, and mercury. The mercaptoacetate solution can also absorb further quantities of mercury mercaptide. S. K. T.

Mercury Ethylmercapto-hydroxides. G. SACHS (*Z. anorg. Chem.*, 1924, **135**, 283—288; cf. preceding abstract).—Dilute mercuric ethylmercaptoacetate solution yields, with potassium hydroxide or with ammonia in ammonium acetate solution, the unstable free base, which immediately decomposes into mercury mercaptide and mercuric hydroxide: $2EtS\cdot Hg\cdot OH = Hg(SEt)_2 + Hg(OH)_2$. Part of the former is precipitated and part is held in solution with the hydroxide, probably in the form of at least two mercapto-hydroxides, the assumption of which is necessary in order to account theoretically for the amount of mercaptide precipitated decreasing with increasing dilution. These mercapto-hydroxides are exceedingly weak bases and their formation appears to be quantitative. S. K. T.

Reversible Catalysis of Unsaturated Hydrocarbons. I. N. ZELINSKY and G. PAVLOV (*Ber.*, 1924, **57**, [*B*], 1066—1070).—The kinetics of the dehydrogenation of *cyclo*hexene under the influence of palladium–asbestos have been examined (cf. A., 1923, i, 767; this vol., i, 665) between 160° and 320°. Dehydrogenation is perceptible at 164° and the product consists of benzene and *cyclo*hexane in the proportion required by the equation $3C_6H_{10} = C_6H_6 + 2C_6H_{12}$. Unchanged *cyclo*hexene was not present in the distillate (cf. Böeseken and Sillevis, A., 1914, i, 254). This decomposition proceeds at temperatures as low as 92°, even in an atmosphere of carbon dioxide, and at temperatures below 130° hydrogen is not given off. In the absence of palladium, *cyclo*hexene is unchanged at 200°. The dehydrogenation curve of *cyclo*hexene between 220° and 300° accordingly corresponds closely with that of a mixture of *cyclo*hexane (2 mols.) and benzene (1 mol.). A similar process of simultaneous oxidation and reduction (cf. Zelinsky and Glinka, A., 1911, i, 870) takes place with *cyclo*hexadiene at 91° in a slow stream of carbon dioxide. In the presence of palladium, no hydrogen is liberated, but benzene and *cyclo*hexane are formed thus: $3C_6H_8 = 2C_6H_6 + C_6H_{12}$. 1 : 4-Dimethyl*cyclo*hexene similarly decomposes at 140° into xylene and dimethyl*cyclo*hexane according to the equation $3C_8H_{14} = C_8H_{10} + 2C_8H_{16}$, whilst at 175—180° under similar conditions menthene is converted into menthane and cymene. Δ^2-Dihydronaphthalene at 130° similarly yields a mixture of naphthalene and tetrahydronaphthalene. This reversible catalysis appears to be characteristic of unsaturated aromatic hydrocarbons containing the double linking in the ring system, but not when the double bond is present in the side-chain. R. B.

Action of Aluminium Sulphide on certain Organic Compounds. G. R. LEVI and G. NATTA (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 350—353).—Aluminium sulphide exerts a dehydrating action on aliphatic compounds and also tends to replace their oxygen by sulphur; with aromatic compounds the former effect predominates. In no case has any marked condensing action been observed.

When passed over aluminium sulphide, benzene vapour at 800—900° yields condensation products such as diphenyl, phenanthrene, and triphenylene; the same products are obtained in about similar yields when benzene vapour at a similar temperature is passed over pumice. At a temperature somewhat below the boiling point of phenol, aluminium sulphide converts the latter completely into phenyl ether. If alcohol vapour is passed at a suitable rate over aluminium sulphide at 330°, ethyl mercaptan is obtained in 46% yield free from ethyl sulphide, the non-reacting alcohol being almost entirely recoverable. Under similar conditions, ether is converted into ethyl sulphide. T. H. P.

Irregularities in the Specific Heats of certain Organic Liquids [Benzene, Ethylbenzene]. J. W. WILLIAMS and F. DANIELS.—(See ii, 589.)

Decomposition of Phenylazoimide in Benzene and in *p*-Xylene. A. BERTHO (*Ber.*, 1924, **57**, [*B*], 1138—1142).—Phenylazoimide is not decomposed by boiling benzene, but is converted by the hydrocarbon at 150—160° into azobenzene and a little aniline, which owes its origin to traces of moisture which could not be entirely excluded. Boiling *p*-xylene decomposes phenylazoimide with formation of *s*-*pp*′-ditolylethane, m. p. 82°, aniline, and traces of azobenzene. At 150—160°, the yields of these products are considerably increased, but the proportion of hydrocarbon still remains below that expected from the yield of the base. H. W.

Orienting Influence of the Thiocyano Group in Aromatic Compounds. F. CHALLENGER and A. D. COLLINS (*J. Chem. Soc.*, 1924, **125**, 1377—1381).—In accordance with the theory of induced alternate polarities, the thiocyano group has been found, from a study of the nitration of phenyl thiocyanate and its *p*-chloro-, *p*-bromo-, *p*-iodo-, and *p*-methyl derivatives, to possess ortho-para directing influence. The predominating, if not exclusive, formation of 2-nitro derivatives of the chloro and bromo compounds shows that the directing influence of the thiocyanate group is more powerful than that of chlorine or bromine. Nitration of *p*-tolyl thiocyanate, however, gives mainly the 3-nitro derivative. Phenyl thiocyanate with nitric and sulphuric acids at 5—10° gives 94% of the theoretical yield of *p*-nitrophenyl thiocyanate, m. p. 133°, which on further nitration at 90° yields 2 : 4-dinitrophenyl thiocyanate. *p*-Tolyl thiocyanate similarly yields at 20° a mixture of 3-nitro-*p*-tolyl thiocyanate and *2-nitro-*p*-tolyl thiocyanate*, yellow needles, m. p. 40°. *p-Bromophenyl thiocyanate*, m. p. 56°, obtained, together with 4 : 4′-dibromodiphenyl sulphide, from *p*-bromoaniline, yields *p*-bromophenyl mercaptan with alcoholic potassium hydrosulphide, and on nitration at 5—10°, *4-bromo-2-nitrophenyl thiocyanate*, long, yellow needles, m. p. 131°, also prepared from 4-bromo-2-nitroaniline, which with potassium hydrosulphide gives potassium thiocyanate and 4-bromo-2-nitrophenyl mercaptan, oxidised to 4 : 4′-dibromo-2 : 2′-dinitrodiphenyl disulphide. The crude nitration product yields traces of a solid bromothiocyanate, m. p. about 95°. *p*-Chlorophenyl thiocyanate, obtained with 4 : 4′-dichlorodiphenyl disulphide from diazotised *p*-chloroaniline, on nitration yields 4-chloro-2-nitrophenyl thiocyanate. p-*Iodophenyl thiocyanate*, m. p. 51—52°, prepared from diazotised thiocyanoaniline (Söderbäck, A., 1920, i, 219) and potassium iodide, with potassium hydrosulphide followed by oxidation, yields 4 : 4′-di-iododiphenyl disulphide and on nitration *p*-nitrophenyl thiocyanate, iodine being displaced by the nitro group. 2 : 4-Dinitrophenyl thiocyanate (or selenocyanate) is also obtained by boiling 1 : 2 : 4-trinitrobenzene with alcoholic potassium thiocyanate (or selenocyanate). 2 : 4-Dinitrophenyl thiocyanate is also obtained, together with 2 : 4 : 2′ : 4′-tetranitrodiphenyl sulphide and disulphide, from 1-chloro-2 : 4-dinitrobenzene. When boiled with alcoholic aniline, the dinitrophenyl thiocyanate is converted into 2 : 4-dinitrodiphenylamine, 2 : 4 : 2′ : 4′-tetranitrodiphenyl sulphide, and a trace of a product, m. p. above 280°, probably the disulphide. Some phenylthiocarbamide was also formed. *p*-Toluidine and an ethereal solution of thiocyanic acid yield *p*-tolylthiocarbamide.

R. B.

Aromatic Hydrocarbons of Low-temperature Tar. O. Kouber (*Ber.*, 1924, **57**, [*B*], 1008—1015; cf. Schütz, A., 1923, i, 195, 1080; Fischer, *ibid.*, 313, 889).—The lowest-boiling fraction of the so-called " motor-oil " fraction (b. p. 190—300°) of low-temperature tar contains benzene derivatives with long side-chains. By a process of sulphonation, separation of the sulphonic acids, and decomposition of these by the usual methods, 1 : 2-dimethyl-4-ethylbenzene, 1 : 2-dimethyl-4-*iso*propylbenzene, and 4-methylhydrindene (previously unknown), which are not present in coke-oven tar, have been isolated together with durene, ψ-cumene, hemimellithene, and hydrindene. 1 : 2-Dimethyl-4-ethylbenzene, d_4^{20} 0·8704, on sulphonation gives a *sulphonic acid*, dense prisms (*sodium salt*, $+1\frac{1}{2}H_2O$), yielding a *sulphonamide*, lustrous needles, m. p. 126—127°. The fraction boiling at 199—202°, d^{15} 0·88—0·89, was sulphonated and the sulphonic acids were distilled with super heated steam, whereby the benzene hydrocarbons were removed leaving an oil, *d* 0·93—0·94, which on sulphonation yielded 4-*methylhydrindenesulphonic acid*, lustrous needles (*sodium* salt, $+1H_2O$, *sulphonamide*, lustrous, white plates, m. p. 175°). The sodium salt on distilling from 70% sulphuric acid at 160—170° with superheated steam yields 4-*methylhydrindene*, having a faint characteristic odour, b. p. 203°, d_4^{20} 0·9350 (*tribromo* derivative, lustrous white needles, m. p. 183°), the constitution of which follows from its oxidation with potassium permanganate to 2 : 6-dicarboxyphenylglyoxylic acid and hemimellitic acid, and its dehydrogenation at 650° to a mixture of indene and methylindene (*benzylidene* derivative, $C_{17}H_{14}$, golden-yellow plates, m. p. 93°). Hydrindene under the same conditions yields indene and a little chrysene, besides resinous products. ψ-Cumene yields a *sulphonic acid*, dense prisms, giving a *sulphonamide*, m. p. 179—180°. *Hemimellithenesulphonamide* has m. p. 194°. 1 : 2-Dimethyl-4-*iso*propylbenzene, d_4^{20} 0·8710, yields a *sulphonic acid*, long needles (*sodium* salt; *sulphonamide*, white needles, m. p. 160—161°), and a *trinitro* derivative, lustrous prisms,

m. p. 119°. On oxidation with nitric acid, it yields o-*xylene*-p-*carboxylic acid*, colourless prisms, m. p. 164—165°, the same acid being obtained by oxidation of 1 : 2-dimethyl-4-ethylbenzene.

R. B.

Low-temperature Tar Oils. R. Weissgerber (*Brennstoff-Chem.*, 1924, **5**, 208—214).—Low-temperature tar, obtained in a rotary oven from gas coal, differs from coke-oven tar in comprising mainly homologues, especially methyl homologues, rather than parent types. The homologous aromatic hydrocarbons are separated by washing with sulphuric acid, followed by sulphonation, advantage being taken of differences in the ease with which they are sulphonated and in the stability of the sulphonic derivatives. The following were identified: durene, 1 : 2 : 3-triethylxylene, 4-methylhydrindene, hydrindene, ψ-cumene, hemimellithene, 2-methyl-*p*-cymene. The fraction b. p. 226—232° gave an aromatic portion having *d* 0·962, which was divided into a picrate-forming portion (d^{15} 1·002) and a non-picrate-forming oil (d^{15} 0·930); 2-methylnaphthalene and 4 : 6-dimethylhydrindene were found in these two portions respectively. Acenaphthene was identified in the neutral oils of b. p. 267—280°. Hydroaromatic compounds were converted, for identification, into their aromatic analogues by catalytic dehydrogenation at 320—330° by means of active charcoal impregnated with 5—10% of platinum, the following being found: decahydronaphthalene, methyldecahydronaphthalene (in a fraction boiling essentially at 203—206°), 1 : 6-dimethyldecahydronaphthalene. Indenes were purified by conversion first into potassium and then into sodium derivatives, and the presence of indene, methylindene, and dimethylindenes (b. p. 225—230°) was proved. Coumarones were also found. A series of ketones were isolated from fractions of b. p. 207—240°, by means of phenylhydrazine, as colourless oils of fruity odour, amongst which *p*-tolyl methyl ketone was identified (as semicarbazone) and methyl heptyl ketone was probably present.

W. T. K. B.

New Preparation of α-Phenylamino-α-phenyl-ethane, -propane, -butane. Resolution of α-Phenylamino-α-phenylethane into its Optical Antipodes and Study of the Rotatory Dispersion of One of These. R. Descamps (*Bull. Soc. chim. Belg.*, 1924, **33**, 269—326).—The secondary alcohols CHPhR·OH (R = Me,Et, or Pr) are converted to the extent of 40—55% into α-phenylamino-α-phenyl-ethane, -propane, or -butane (cf. A., 1904, i, 663) by mixing with 4 mols. of aniline and 1% of *p*-toluenesulphonic acid and heating for 8—9 hours at 170—190°. Styrene is formed as a by-product to the extent of 14—16%. Reychler's camphorsulphonic acid may also be used as the catalyst. The following constants are recorded: α-Phenylethyl alcohol, m. p. 20·1°, b. p. 96°/15 mm., 93·75°/12 mm., d^{0}_{4} 1·0290, d^{15}_{4} 1·0178, d^{20}_{4} 1·0129, n^{20}_{α} 1·5232, n^{20}_{D} 1·5275, n^{20}_{β} 1·5388, n^{20}_{γ} 1·5485; α-phenylamino-α-phenylethane, CHPhMe·NHPh, long needles, m. p. 26·4°, b. p. 178°/15 mm., 137°/2 mm., d^{0}_{4} 1·0610, d^{15}_{4} 1·0492, d^{20}_{4} 1·0453, d^{100}_{4} 0·9819, n^{20}_{α} 1·5939,

n_D^{20} 1·6004, n_β^{20} 1·6178, n_γ^{20} 1·6332; nitrosoamine, b. p. 168—169°/2 mm. (slight decomp.), d_4^0 1·1172, d_4^{20} 1·1010, n_α^{20} 1·5881, n_D^{20} 1·5948, n_β^{20} 1·6118. α-Phenylamino-α-phenylpropane, CHPhEt·NHPh, pale yellow oil, b. p. 192°/20 mm., 176·6°/10·5 mm., 148°/3 mm., d_4^0 1·0501, d_4^{15} 1·0383, d_4^{20} 1·0343, n_α^{20} 1·5877. α-Phenylamino-α-phenylbutane, CHPhPr·NHPh, nearly colourless oil, b. p. 209·5°/30 mm., 187·8°/12·5 mm., 167°/3·75 mm., d_4^0 1·0353, d_4^{15} 1·0239, d_4^{20} 1·0190, n_α^{20} 1·5798. α-Phenylamino-α-phenylethane was resolved by crystallisation of its camphorsulphonate from a mixture of benzene and dry ether, the more sparingly soluble salt being recrystallised from benzene until optically pure. The pure salt had $[\alpha]_{5893}^{20}+104·68°$ and $[\alpha]_{4358}^{20}+243·02°$ for an 11·73% alcoholic solution. The active base (one antipode only was isolated) had m. p. 49·2°, b. p. 130·2°/1·5 mm., 140°/3 mm., 170·5°/12 mm., d_4^{50} 1·0253, d_4^{100} 0·9879; $[\alpha]_D^{50}$ −0·12° and $[\alpha]_D^{100}$ +5·15° (liquid base); its hydrochloride had m. p. 199—200°.

A large number of observations of optical rotatory power of the camphorsulphonate, the hydrochloride, and the free base in different solvents and at different concentrations and temperatures are recorded. The salts are dextrorotatory, but the sign of rotation of the free base depends on the solvent, concentration, and temperature. Between the limits λ 5893 and λ 4358, the curves for the rotatory dispersion of the camphorsulphonate of the active base in various solvents and for the hydrochloride in ethyl alcohol are all of the simple type; the curves for the base, fused or in solution, are either of the complex normal type or more often of the complex abnormal type; the curve for a 4·09% solution of the base in ethylene dibromide was the only one of these of simple type; the rotatory power of the base in various concentrations in absolute alcohol at 50° is a function of the concentration by weight. The rule of Darmois concerning the rotatory dispersion of mixtures in various proportions of two active substances holds for these solutions.

Two possible explanations of these results are discussed, namely, the presence of an absorption band in some part of the spectrum, or the existence in the liquid of two active substances in equilibrium. The former of these is rejected on account of the simple form of rotatory dispersion shown by the camphorsulphonate, which, having a more complex molecule than the free base, would not be expected to have an absorption band more remote in the ultraviolet. The conception of the presence of two active substances is, on the other hand, supported by all the experimental data. It is suggested that two dynamic isomerides of the base are present, the salts being derived from one of them. G. M. B.

Absorption Spectrum of Naphthalene Vapour. V. HENRI and H. DE LÁZLÓ.—(See ii, 513.)

Sulphonation of Fluorene. C. COURTOT and R. GEOFFROY (*Compt. rend.*, 1924, **178**, 2259—2262).—Fluorene-2-sulphonic acid is obtained as silvery leaflets (m. p. 154—155°) by the action of chlorosulphonic acid on fluorene. It gives a *sulphochloride*,

m. p. 164°, a *sulphonamide*, m. p. 211°, and, when further sulphonated with cold chlorosulphonic acid or 95% sulphuric acid, a single disulphonic acid identical with the α-compound obtained by Schmidt and others (cf. A., 1912, i, 695). This disulphonic acid gives a *disulphochloride*, m. p. 225—226°, and a *disulphonamide*, m. p. 305°. Various proofs that it is the 2 : 7-derivative are adduced.

W. T. K. B.

Preparation of Chlorinated Amines. DURAND et HUGUENIN S.A. (Brit. Pat. 217753).—Highly chlorinated hydroaromatic compounds containing nitrogen (chloroketimines; cf. Brit. Pats. 193843 and 198676, this vol., i, 631) are reduced (*e.g.*, with zinc and hydrochloric acid, calcined sodium sulphide in methyl or ethyl alcohol, or ethyl alcohol alone), hydrolysis being avoided. The preparation of the following is described: tetrachloro- and pentachloro-aniline, 1 : 3 : 4-trichloro-β-naphthylamine, 2 : 3 : 4-trichloro-α-naphthylamine (m. p. 162°), 1 : 3(or 3 : 4- ?)-dichloro-β-naphthylamine (m. p. 93·5°), dichloro- and 2 : 3 : 4-trichloro-α-aminoanthraquinone (m. p. 204° and 210°, respectively).

W. T. K. B.

Action of Mercuric Acetate on *m*-Toluidine and on *p*-Chloroaniline. L. VECCHIOTTI (*Gazzetta*, 1924, **54**, 411—425; cf. A., 1919, i, 103; 1921, i, 902).—The action of mercuric acetate on *m*-toluidine in aqueous solution yields: (1) *m*-toluidinemercuriacetate, (2) the *m*-toluidinedimercuriacetate [Me : NH_2 : Hg : Hg = 1 : 3 : 4 : 6] obtained in methyl-alcoholic solution by Schrauth and Schoeller (A., 1912, i, 930), and (3) the 1 : 3 : 2 : 5-isomeride of (2).

In the action of mercuric acetate on the three nitroanilines (cf. Jackson and Peakes, A., 1908, i, 523), the mercuriacetoxy group always assumes the para-position with respect to the amino group if such position is free, or alternatively the ortho-position, a second mercuriacetoxy group then also assuming an ortho-position. Similarly, the action of mercuric acetate on *p*-chloroaniline results in the introduction of a mercuriacetoxy group in the ortho-position to the amino group.

m-Toluidinedimercuriacetate [1 : 3 : 4 : 6] forms white laminæ, m. p. 191°, and its *acetyl* derivative, $NHAc{\cdot}C_6H_2Me(Hg{\cdot}OAc)_2$, tufts of needles, m. p. 250°; the latter gives 4 : 6-dibromoaceto-*m*-toluidide, m. p. 168° (cf. Nevile and Winther, T., 1880, **37**, 433). m-*Toluidinedimercurihydroxide*, $NH_2{\cdot}C_6H_2Me(Hg{\cdot}OH)_2$, forms unstable, white laminæ, the *chloride* lamellar crystals, m. p. 195°, and the *bromide*, small, mammillary crystals, m. p. 210°.

m-*Toluidine*-6-*mercuriacetate*, $NH_2{\cdot}C_6H_3Me{\cdot}Hg{\cdot}OAc$, crystallises in small needles, m. p. 176°, and its *acetyl* derivative, m. p. 192° (impure), gives 6-bromoaceto-*m*-toluidide, m. p. 113—114° (cf. Nevile and Winther, *loc. cit.*). m-*Toluidine*-2 : 5-*dimercuriacetate* forms lustrous white needles, m. p. 170°; the corresponding m-*acetotoluidide*, silky, white needles, m. p. 183—184°; the *dimercurihydroxide*, a white, lamellar mass, decomposing at 220°; the *chloride*, acicular crystals, m. p. 239—240° (decomp.), and the *bromide*, white lamellæ, decomposing at 150°.

4-*Chloroaniline*-2-*mercuriacetate*, $NH_2·C_6H_3Cl·Hg·OAc$, crystallises in long, prismatic needles, m. p. 207°. The corresponding *mercurihydroxide* forms a white precipitate, and the *chloride*, minute needles, decomposing at 205°. p-*Chloroacetanilide*-2-*mercuriacetate* forms long needles, m. p. 200°, and is converted by chlorination into 2 : 4-dichloroacetanilide.

2-*Mercuridi*-p-*chloroaniline*, $Hg(C_6H_3Cl·NH_2)_2$, obtained by the action of sodium thiosulphate on *p*-chloroanilinemercuriacetate, forms regular, white mammillæ, decomposing at 130°. T. H. P.

Amines. IX. Some Chemical Properties of Aminoacetodiphenylamide. E. B. Kelsey (*J. Amer. Chem. Soc.*, 1924, **46**, 1693—1700; cf. A., 1920, i, 681; 1922, i, 1141).—Attempts have been made, by the methods previously described, to prepare thiocarbimides of acetoethylanilide and acetophenylanilide (acetodiphenylamide), in which intramolecular change to thiohydantoins is precluded, but the carbethoxydithiocarbamate obtained undergoes profound decomposition and no mustard oil could be obtained. *Chloroacetoethylanilide*, $NPhEt·CO·CH_2Cl$, white needles, b. p. 188°/35 mm., from ethylaniline and chloroacetyl chloride, with aqueous or alcoholic ammonia yields only the *triphenylethylamide* of triglycolamidic acid, $(NPhEt·CO·CH_2)_3N$, colourless crystals, m. p. 119°. *Chloroacetodiphenylamide*, colourless plates, with alcoholic ammonia after 4 days yields, on evaporation of the alcohol and pouring into water, a viscous mass, converted with alcohol and hydrogen chloride into the *hydrochloride* of the *didiphenylamide* of diglycolamidic acid, $(NPh_2·CO·CH_2)_2NH,HCl$, white plates, m. p. 240—245° (decomp.) [*benzoyl* derivative, $(NPh_2·CO·CH_2)_2NBz$, glistening crystals, m. p. 200°], whilst the filtrate on evaporation yields *aminoacetodiphenylamide hydrochloride*, $NPh_2·CO·CH_2NH_2,HCl$ [*nitrate*, plates, m. p. 211—214° (decomp.)]. The *hydrated base*, yellow oil ($+1H_2O$), after 2 months in a vacuum desiccator, gave the anhydrous *base*, long, silky needles, m. p. 53—55°. The didiphenylamide of diglycolamidic acid is also formed by the prolonged action of aqueous ammonia on chloroacetodiphenylamide. The action of ethyl chloroformate on aminoacetodiphenylamide in benzene gives *carbethoxyaminoacetodiphenylamide*, $NPh_2·CO·CH_2·NH·CO_2Et$, silky needles, m. p. 64—65°; the *acetyl*, m. p. 157—158°, *chloroacetyl*, m. p. 117—118°, and *benzoyl*, m. p. 152°, derivatives of aminoacetodiphenylamide are prepared similarly. Carbon disulphide in alcoholic solution converts aminoacetodiphenylamide into a *dithiocarbamate*, m. p. 150—155° on sudden heating (orange *silver* salt), which in hot alcoholic solution loses hydrogen sulphide and slowly deposits pale yellow crystals of the *thiocarbamide*, $(NPh_2·CO·CH_2·NH)_2CS$, m. p. 260° (decomp.), also obtained as white crystals, m. p. 258—260°, by the action of thiocarbonyl chloride on aminoacetodiphenylamide. Treatment with ethyl chloroformate in ether converts the dithiocarbamate into *carbethoxyaminoacetodiphenylamide dithiocarbamate*,

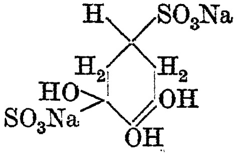
$NPh_2 \cdot CO \cdot CH_2 \cdot NH \cdot CS \cdot S \cdot CO_2Et$, pale yellow needles, sintering at 101°, m. p. 112—115° (decomp.), which on distillation under reduced pressure decomposes, giving a black tar. Hydrochloric acid decomposes aminoacetodiphenylamide dithiocarbamate, but without liberation of hydrogen sulphide, giving aminoacetodiphenylamide hydrochloride, and the filtrate on treatment with mercuric chloride deposits the *mercuric* salt of the dithiocarbamate. R. B.

Nitro Derivatives of *p*-Aminophenol and *p*-Aminophenoxyacetic Acid. A. GIRARD (*Bull. Soc. chim.*, 1924, [iv], **35**, 772—779).—By nitrating *p*-acetamidophenol with the theoretical amount of nitric acid in sulphuric acid at —5° with very rapid agitation, a quantitative yield of 2-nitro-4-acetamidophenol is obtained (cf. Reverdin, A., 1905, i, 51, 430; 1906, i, 165). Nitration of *p*-acetamidophenyl acetate at —5° to 5°, and finally at 15°, by a modification of Hähle's method (A., 1891, 430) gives 3-nitro-4-acetamidophenol in 97% of the theoretical yield; further nitration with sulphuric acid and potassium nitrate at 0—10° gives a product containing 95% of 2 : 3-dinitro-4-acetamidophenol and 5% of 3 : 6-*dinitro*-4-*acetamidophenol*, fine lemon-yellow needles, m. p. 144°, which is hydrolysed by sulphuric acid to 3 : 6-*dinitro*-4-*aminophenol*, fine, nearly black needles with coppery lustre, m. p. 166°, subliming at higher temperatures. When diazotised and decomposed with potassium iodide, the dinitroaminophenol yields 4-*iodo*-3 : 6-*dinitrophenol*, lemon-yellow spangles, m. p. 112°. 3 : 6-Dinitro-4-acetamidophenol, on further nitration, yields 2 : 3 : 6-trinitro-4-acetamidophenol, whilst its silver salt with methyl iodide yields 2 : 5-dinitro-4-acetanisidide (Reverdin and Bucky, A., 1906, i, 748).

2-*Nitro*-4-*acetamidophenoxyacetic acid*, reddish-yellow needles, m. p. 205°, is obtained by nitration of *p*-acetamidophenoxyacetic acid with sulphuric acid and potassium nitrate at —5° to 0° (cf. Howard, A., 1898, i, 29), whilst nitration in acetic acid at 0° yields 3-*nitro*-4-*acetamidophenoxyacetic acid*, lemon-yellow needles, m. p. 174°, yielding the nitroamino acid of Reverdin (A., 1909, i, 913) on acid hydrolysis. Further nitration with nitric and sulphuric acids gives the dinitro-acid, m. p. 207°, obtained by Howard, which is now shown to be 2 : 3-*dinitro*-4-*acetamidophenoxyacetic acid* by the synthesis of its *ethyl* ester, m. p. 155°, from silver 2 : 3-dinitro-4-acetamidophenoxide and ethyl bromoacetate. R. B.

Oxidation Induced by Metals. J. ALOY and A. VALDIGUIÉ (*Bull. Soc. chim.*, 1924, [iv], **35**, 792—794; cf. A., 1923, ii, 552).—The oxidation of quinol is catalysed by uranium acetate with production of an intense red coloration (cf. A., 1903, ii, 581; 1905, ii, 616) and precipitation of quinhydrone. Traces of hydrochloric acid do not affect the reaction, but the formation of quinhydrone is prevented by an excess of mineral acid. In the presence of ammonium chloride, the catalytic oxidation of quinol yields a red colouring matter which resembles the quinoneimides in its reactions. Salts of manganese, iron, copper, vanadium, uranium, mercury, lead, and cobalt catalyse the reaction by fixing atmospheric oxygen, whilst magnesium, aluminium, cadmium, zinc, and nickel are inactive. The alkali salts are also inactive except those possessing a peroxidic structure, such as persulphates, perborates, iodates, and periodates. R. B.

Tautomerism of Phenols. VI. Pyrogallol and Hydroxyquinol. W. Fuchs and B. Elsner (*Ber.*, 1924, 57, [*B*], 1225—1231).—Pyrogallol is converted by very protracted heating with an aqueous solution of sodium hydrogen sulphite (2 mols.) into the *sodium hydrogen sulphite* additive compound of *sodium* 3 : 4-*dihydroxy*-5-*keto*-1 : 2 : 5 : 6-*tetrahydrobenzene*-1-*sulphonate* (annexed formula). Under similar conditions but with greater rapidity, hydroxyquinol gives the *sodium hydrogen sulphite* additive compound of *sodium* 5 : 6-*dihydroxy*-3-*keto*-1 : 2 : 3 : 4-*tetrahydrobenzene*-1-*sulphonate*. The compounds readily lose a molecule of sodium hydrogen sulphite when acted on by hydrogen peroxide, and yield respectively *sodium* 3 : 4-*dihydroxy*-5-*keto*-1 : 2 : 5 : 6-*tetrahydrobenzenesulphonate* and *sodium* 5 : 6-*dihydroxy*-3-*keto*-1 : 2 : 3 : 4-*tetrahydrobenzenesulphonate*, which are isolated by taking advantage of their solubility in acetone. The reaction with ferric chloride is similar to that of pyrocatechol. The action of diazomethane in the presence of acetone yields a *monomethyl* derivative in each case. The presence of the ketonic group in the compound derived from hydroxyquinol is established by the isolation of a *phenylhydrazone*, $C_{12}H_{13}O_5N_2SNa$. Bromine in anhydrous solvents has no action on the mono- or di-products; in aqueous solution, a maximal absorption of one molecular proportion of halogen is observed. H. W.



New Catalytic-electrolytic Method of Reduction. F. Ishiwara (*Ber.*, 1924, 57, [*B*], 1125—1126).—The apparatus consists of a round-bottomed vessel which can be suspended so as to permit continuous agitation and through which a current of hydrogen or other gas can be passed. It is pierced near the base by a hole provided with a rubber stopper through which a palladium cathode passes. An opening in the top of the vessel carries a small porous cell containing dilute hydrochloric acid and a nickel anode. During reduction, a current of hydrogen is passed into the vessel. The reducing action of the catalyst appears to be strengthened greatly by the passage of the electric current, but reduction is also effected partly directly at the cathode. 4-α-Methylaminoacetylpyrocatechol hydrochloride is smoothly reduced to 4-α-hydroxy-β-methylaminoethylpyrocatechol, $NHMe\cdot CH_2\cdot CH(OH)\cdot C_6H_3(OH)_2$, m. p. 230°, the yield being 96% of the theoretical. 4-p-*Carbethoxyanilinoacetylpyrocatechol*, $CO_2Et\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot C_6H_3(OH)_2$, m. p. 201°, is prepared by the action of ethyl *p*-aminobenzoate on 4-chloroacetylpyrocatechol in boiling alcoholic solution. H. W.

History of Ketopinic Acid and "Norcamphane-1-carboxylic Acid." P. Lipp (*Ber.*, 1924, 57, [*B*], 1071).—Since the acid obtained by Wedekind from ketopinic acid (this vol., i, 639) still contains two methyl groups, the name *apo*camphane-1-carboxylic acid is preferred, but this name has been assigned by Wedekind to an acid of unknown constitution obtained by Bredt and May (A., 1910, i, 32). The author obtained *apo*camphanonitrile from bromocamphanehydroxamyl bromide (A., 1914, i, 305), and this on hydrolysis yields quantitatively the *apo*camphane-1-carboxylic acid, m. p. 221—222°, described by Wedekind. In Wedekind's papers (this vol., i, 639; 1923, i, 346) Komppa's synthesis of pinophanic acid (A., 1911, i, 642), the acid hydrolysis product of ketopinic acid, has been overlooked. R. B.

Action of Metals on Acid Chlorides in presence of Ether. H. P. KAUFMANN and C. FUCHS (*Arch. Pharm.*, 1924, **262**, 119—125).—Zinc, benzoyl chloride, and ether interact to yield ethyl chloride and an oil, from which a complex *compound*,

$$Zn(Ph{\cdot}CO_2Et)_6Cl_2,$$

crystallises after some time in colourless needles; it is decomposed into its components by water. The oily mother-liquor is ethyl benzoate containing an amorphous *compound*, $C_{16}H_{12}O$, m. p. 125—130°. The relative amount of the latter increases as the proportion of ether used decreases. Two reactions appear to be taking place, in one of which co-ordination compounds containing ether are produced which then undergo a complex change; the zinc chloride formed brings about the formation of ethyl benzoate (cf. Descudé, A., 1903, i, 735; Blaise, A., 1905, i, 255). Aluminium chloride has the same effect but aluminium itself does not behave like zinc. Acetyl chloride, ether, and zinc yield ethyl chloride, ethyl acetate, and an amorphous yellow substance, but no metallic complex compound. Phthalyl chloride treated in the same way (and heated) gives diethyl phthalate, phthalic anhydride (presumably by partial esterification and subsequent scission of ethyl chloride), a little amorphous, yellow substance and a *compound*, $C_7H_7O_2$, m. p. 182°. Anisole, benzoyl chloride, and zinc react vigorously to yield chiefly *p*-methoxybenzophenone; some benzaldehyde is formed by reduction of the benzoyl chloride, the hydrogen chloride formed in the main reaction attacking the unused zinc (cf. Blaise, *loc. cit.*).
W. A. S.

Application of the Principle of the Schotten-Baumann Benzoylation Process to Acid Anhydrides. W. AUTENRIETH and G. THOMAE (*Ber.*, 1924, **57**, [*B*], 1002—1008).—The acylation of phenols may be readily effected by acid anhydrides in the presence of sodium hydroxide. The best yields of ester are obtained with double the theoretical quantity of sodium hydroxide; excess of anhydride does not appreciably increase the yield. Acylation of aniline and other bases proceeds best in the absence of sodium hydroxide, and the yields are diminished by excess of this reagent and increased by excess of anhydride. Solid anhydrides must be melted, as the reaction only proceeds in the liquid phase. Anhydrides the melting points of which lie above 100° scarcely react, but *m*-nitrobenzoic anhydride, m. p. 159°, which melts under boiling water, gives 25% of the theoretical yield of *phenyl* m-*nitrobenzoate*, laminæ, m. p. 99°, and 16% of the theoretical yield of *m*-nitrobenzanilide. Alcohols react much less readily than the phenols and only small amounts of the alkyl esters are formed. Although *p*-bromobenzoyl chloride reacts with aqueous methyl alcohol when the concentration of the alcohol is as low as 0·1% (cf. A., 1920, ii, 776), with ethyl alcohol of less than 5% concentration, and sodium hydroxide weaker than 10—15%, *p*-bromobenzoic anhydride is formed almost exclusively. *n*-Propyl and *iso*-amyl alcohols, secondary and tertiary alcohols, borneol, menthol, sabinol, and santalol behave similarly, whilst benzyl alcohol, glycerol, phenol, cresols, and eugenol yield the corresponding *p*-bromobenzoates. Since the anhydride is not formed when *p*-bromobenzoyl chloride and sodium *p*-bromobenzoate are heated with dilute sodium hydroxide at 45°, it is concluded that the formation of *p*-bromobenzoic anhydride under the conditions given is due to the catalytic effect of the alcohols in question. The following esters and anilides were prepared by this method: phenyl benzoate, *p*-tolyl benzoate, resorcinyl benzoate, phloroglucinol tribenzoate, phenyl phenylacetate, phenyl *p*-toluate, *p*-tolyl *p*-toluate, *resorcinyl diphenylacetate*, $C_6H_4(CO_2{\cdot}CH_2Ph)_2$, needles, m. p. 62—63°, *resorcinyl di-*p-*toluate*, $C_6H_4(CO_2{\cdot}C_6H_4Me)_2$, long prisms, m. p. 137—138°, *benzopiperidide*, dense prisms, m. p. 49°, p-*toluopiperidide*, lustrous plates, m. p. 55—58°, benzanilide, α-phenylacetanilide, *p*-toluanilide, benzo-*p*-toluidide, and phenylaceto-*p*-toluidide. R. B.

Compound of "Benzocaine" and Iodine. L. E. Warren (*Repts. Lab. Amer. Med. Assoc.*, 1923, **16**, 97—99).—"Benzocaine" [ethyl *p*-aminobenzoate] forms a brown compound, probably containing 2 equivalents of iodine per mol., when iodine is added to its solution in dilute hydrochloric acid.

Chemical Abstracts.

Alcoholysis of Esters of αβ-Unsaturated Acids and of the Corresponding Saturated Analogues. B. Dasannacharya.—(See i, 937.)

Addition of Methyl Hypobromite to certain Ethylene Derivatives. J. B. Conant and E. L. Jackson (*J. Amer. Chem. Soc.*, 1924, **46**, 1727—1730).—The action of bromine on a solution of cinnamic acid in methyl alcohol containing 15% of water gives dibromocinnamic acid and α-bromo-β-methoxy-β-phenylpropionic acid, $OMe{\cdot}CHPh{\cdot}CHBr{\cdot}CO_2H$, m. p. 182—183°, an identical product with this melting point being obtained on repeating Schrauth's work (A., 1922, i, 1125). Similarly, phenyl styryl ketone yields α-bromo-β-methoxy-β-phenylpropiophenone,

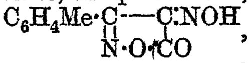
$$OMe{\cdot}CHPh{\cdot}CHBr{\cdot}COPh,$$

together with a little dibromide. The reaction apparently involves the formation of methyl hypobromite, and the mechanism of the addition is probably as follows: $Br_2+MeOH \rightleftharpoons MeOBr+HBr$; $>C:C<+MeOBr \longrightarrow >C(OMe){\cdot}CBr<$ (cf. Read and Andrews, T., 1921, **119**, 1774). R. B.

Unsaturated Compounds. XI. Action of Free Hydroxylamine on Cinnamic Acid and its Nuclear Homologues. T. Posner and G. Schreiber (*Ber.*, 1924, **57**, [*B*], 1127—1137).—The action of hydroxylamine on cinnamic acid yields primarily β-hydroxylamino-β-phenylpropionic acid, which further undergoes reduction and oxidation to β-amino-β-phenylpropionic acid and β-oximino-β-phenylpropionic acid; the latter substance is unstable and loses carbon dioxide with formation of acetophenoneoxime or water with production of phenyl*iso*oxazolone. Extension of these observations to *o*-, *m*-, and *p*-methylcinnamic acids shows that the additive capacity of the different acids for hydroxylamine is inversely proportional to the strength of the acids and that the hydroxylamino-acid is most readily reduced to the corresponding amino-acid when the former is produced with the greatest difficulty. Differences in the readiness of addition of hydroxylamine are not observed when the acids are replaced by their methyl esters.

The determination of the dissociation constants of the acids is rendered difficult by their very sparing solubility in water. The following data are recorded with reserve: *o*-methylcinnamic acid (2·53), cinnamic acid (2·19), *p*-methylcinnamic acid (1·82), *m*-methylcinnamic acid (1·57).

β-Hydroxylamino-β-*o*-tolylpropionic acid is oxidised by ammoniacal silver nitrate solution to 3-o-*tolyl*iso*oxazolone*, m. p. 89—91°, which yields 4-*oximino*-3-o-*tolyl*iso*oxazolone*,

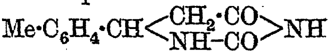


$$\begin{array}{l} C_6H_4Me\cdot C\text{——}C{:}NOH \\ \qquad\qquad\;\, \| \qquad\quad\;\; | \\ \qquad\qquad\;\, N\cdot O\cdot CO \end{array}$$

, m. p. 127—128°. β-*Amino*-β-o-*tolylpropionic acid*, m. p. 242° (decomp.), is converted into the *benzoyl* derivative, m. p. 197°, and β-*carbamido*-β-o-*tolyl-propionic acid*,

$$C_6H_4Me\cdot CH(NH\cdot CO\cdot NH_2)\cdot CH_2\cdot CO_2H,$$

m. p. 182—183°; the latter substance passes when heated at 230—235° into 4-o-*tolyldihydrouracil*,



$$Me\cdot C_6H_4\cdot CH<\begin{matrix} CH_2\cdot CO \\ NH-CO \end{matrix}>NH$$

, m. p. 223—225°. β-*Amino*-β-o-*tolylpropionanilide*, m. p. 135—136°, and *methyl* o-*tolyl ketoxime*, m. p. 61°, are also described. The following compounds are prepared from *m*-methylcinnamic acid: β-*Hydroxylamino*-β-m-*tolylpropionic acid*, m. p. 158°; 3-m-*tolyl*iso*oxazolone*, m. p. 82—83°; 4-*benzeneazo*-3-m-*tolyl*iso*oxazolone*, m. p. 142—143°, which is converted by phenylhydrazine into *benzeneazo*-m-*tolylphenylpyrazolone*, m. p. 141°; β-*amino*-β-m-*tolylpropionic acid*, m. p. about 225° (decomp.), according to the rate of heating; β-*benzoylamino*-β-m-*tolylpropionic acid*, m. p. 154·5°; β-*carbamido*-β-m-*tolylpropionic acid*, m. p. 89°; 4-m-*tolyldihydrouracil*, m. p. 191°; β-*amino*-β-m-*tolylpropionanilide*, m. p. 106—107°; methyl *m*-tolyl ketoxime, m. p. 57°; β-*hydroxylamino*-β-m-*tolylpropionhydroxamoxime hydrate*, $C_6H_4Me\cdot CH(NH\cdot OH)\cdot CH_2\cdot C(NH\cdot OH)_2\cdot OH$. *p*-Methylcinnamic acid gives rise to the following derivatives: 4-*Benzeneazo*-3-p-*tolyl*iso*oxazolone*, m. p. 176°; *benzeneazo*-p-*tolylphenylpyrazolone*, m. p. 173°; β-*amino*-β-p-*tolylpropionanilide*, m. p. 127—128°; β-*hydroxylamino*-β-p-*tolylpropionhydroxamoxime hydrate*, m. p. 128—129°.

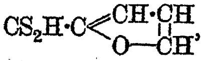
Rapid chlorination of *m*-xylene at its boiling point under the influence of ultra-violet light until the gain in weight corresponding with the absorption of one atomic proportion of chlorine is attained gives a mixture of unchanged *m*-xylene, *m*-xylyl chloride, and *m*-xylylene dichloride, m. p. 33—34°. H. W.

Substituted Salicylic Acids. IV. H. P. KAUFMANN and M. THOMAS (*Arch. Pharm.*, 1924, **262**, 117—119; cf. i, 175).—Chloroacetylsalicylic acid interacts in alcohol solution with gaseous ammonia in presence of copper, yielding *glycylsalicylic acid*, $NH_2{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H$, the *hydrochloride* of which has m. p. 70°; the *ammonium* salt is described. When potassium methyl salicylate and glycyl chloride hydrochloride (Fischer, A., 1905, i, 863, 892) are heated in benzene, the *methyl* ester of the above is obtained, needles, m. p. 195°. *Hippurylsalicylic* (*benzoylglycylsalicylic*) *acid*, m. p. 119°, is similarly produced from sodium salicylate and hippuryl chloride (Fischer, *loc. cit.*); its *phenyl* ester, from the potassium compound of phenyl salicylate (salol), has m. p. 45°. W. A. S.

Method of Preparation of Organic Dithio-acids. G. BRUNI and T. G. LEVI (*Gazzetta*, 1924, **54**, 389—395).—Organic dithio-acids of the aromatic series may be readily obtained by the action of yellow ammonium sulphide on the corresponding aldehydes; the presence of alcohol as a solvent of the aldehyde is sometimes advantageous, but is not necessary (cf. Bloch and Höhn, A., 1910, i, 256; White, P., 1914, 37).

Dithiosalicylic acid, its zinc and lead salts, and the corresponding disulphide (Bloch and Höhn, *loc. cit.*) have been prepared in this way, also dithioanisic acid and its zinc and lead salts (the disulphide has m. p. 150°; Bloch and Höhn found 161—163°), and the following compounds. *Dithioprotocatechuic acid*,

$$C_6H_3(OH)_2{\cdot}CS_2H,$$

forms a violet-red oil, its *zinc* salt being reddish-brown and its *lead* salt forming unstable, reddish-brown crystals. *Dithiovanillic acid*, $OMe{\cdot}C_6H_3(OH){\cdot}CS_2H$, forms a red, crystalline mass, its *zinc* and *lead* salts orange-yellow crystals, and the corresponding *disulphide* red crystals. *Dithiopiperonylic acid*, $CH_2O_2{:}C_6H_3{\cdot}CS_2H$, prepared from piperonaldehyde, forms a red, crystalline mass, its *zinc* salt orange-red needles, its *lead* salt orange crystals, and the *disulphide* greenish-yellow crystals, m. p. 146°. *Dithiocinnamic acid* forms a red oil and its *zinc* and *lead* salts red crystals. *Dithiopyromucic acid*,  $CS_2H{\cdot}C{<}\begin{array}{l}CH{\cdot}CH\\ \quad\;\;\|\\ O{-}CH\end{array}$, forms a stable, violet-red oil, its *zinc* and *lead* salts orange crystals, and its *disulphide* purple-red crystals, m. p. 89·5—90·5°.

The zinc salts of the above acids act as accelerators in the vulcanisation of rubber and more pronounced effects are shown by the disulphides, which, if used in large proportion or if vulcanisation is protracted, exhibit an auto-accelerating action.

The action of ammonium polysulphide in excess on aliphatic aldehydes, diluted with a suitable solvent, furnishes an excellent method for the rapid preparation of the corresponding thioaldines. Formaldehyde, however, behaves differently, the resulting product being a white, crystalline base containing nitrogen and sulphur which is being investigated. T. H. P.

Nitro- and Amino-iodohydroxybenzoic Acids. P. Brenans and C. Prost (*Compt. rend.*, 1924, **178**, 1824—1826).—The action of iodine on 5-nitrosalicylic acid ($CO_2H:OH:NO_2=1:2:5$) in presence of mercuric oxide yielded 3-*iodo*-5-*nitrosalicylic acid*, white needles, m. p. 228° (decomp.), together with 2 : 6-*di-iodo*-4-*nitrophenol*, needles, m. p. 155°; these compounds were separated by fractional crystallisation of their barium and sodium salts. Reduction of the former substance by stannous chloride yields 3-*iodo*-5-*aminosalicylic acid hydrochloride*, white needles, from which the *acid*, silvery plates, decomp. 215°, is prepared by the action of sodium acetate. The hydrochloride on treatment with amyl nitrite affords 3-iodosalicylic acid (cf. A., 1923, i, 797). 5-*Iodo*-3-*nitrosalicylic acid*, pale yellow needles, m. p. 105°, mixed with some 4 : 6-*di-iodo*-2-*nitrophenol*, yellow needles, m. p. 98°, was obtained from 3-nitrosalicylic acid in a similar manner to its isomeride. Its *ethyl* ester forms pale yellow plates, m. p. 129°; the acid on reduction yields 5-*iodo*-3-*aminosalicylic acid*, brilliant white needles, changing at 190—200° without melting; treatment with amyl nitrite affords 5-iodosalicylic acid (*loc. cit.*). 5-*Iodo*-3-*nitro*-4-*hydroxybenzoic acid*, small lemon-yellow needles, m. p. 240° (decomp.), is formed together with 4 : 6-di-iodo-2-nitrophenol from iodine and 3-nitro-4-hydroxybenzoic acid; *ethyl* ester, yellow needles, m. p. 105°; corresponding *amino-acid*, needles, decomp. 155°, *hydrochloride*, white needles. H. J. E.

o-Benzoylbenzoic Acids containing Fluorine, Iodine, and Sulphur. F. C. Hahn and E. E. Reid (*J. Amer. Chem. Soc.*, 1924, **46**, 1645—1653).—Aromatic fluorine derivatives readily condense with phthalic anhydride in the presence of aluminium chloride, yielding white fluorobenzoyl-*o*-benzoic acids which on heating with sulphuric acid at 100—150° are converted into pale yellow anthraquinones. Fluorobenzene gives in 90% of the theoretical yield *p*-fluorobenzoyl-*o*-benzoic acid, m. p. 137—137·5° (*methyl* ester, m. p. 93·5°; *ethyl* ester, m. p. 80·5°; *propyl* ester, b. p. 200°/8 mm.; *butyl* ester, b. p. 225°/8 mm.), yielding *p*-hydroxybenzoyl-*o*-benzoic acid on hydrolysis with sodium hydroxide, p-*fluorobenzyl*-o-*benzoic acid*, m. p. 148—149°, on reduction by Scholl's method (A., 1911, i, 1007) and β-fluoroanthraquinone, m. p. 203—204°, on treatment with sulphuric acid. From *p*-fluorotoluene is obtained, in 96% of the theoretical yield, 5-*fluoro*-2-*methylbenzoyl*-o-*benzoic acid*, m. p. 150° (*methyl* ester, m. p. 79·5—80°; *ethyl* ester, oil) condensing to 4-*fluoro*-1-*methylanthraquinone*, m. p. 155—156°, which is oxidised by nitric acid to 4-fluoroanthraquinone-1-carboxylic acid, m. p. about 250°, and losing carbon dioxide to give probably α-fluoroanthraquinone, m. p. 128—129°. Similarly, *o*-fluorotoluene gives 96% of the theoretical yield of 3-*fluoro*-4-*methylbenzoyl*-o-*benzoic acid*, m. p.

153·5—154° (*methyl* ester, m. p. 108°; *ethyl* ester, m. p. 74°), oxidised by alkaline permanganate to 3-*fluorobenzophenone*-2′ : 4-*dicarboxylic acid*, m. p. 183—184° (sintering at 175°), and condensing to 3-*fluoro-2-methylanthraquinone*, m. p. 172°, oxidised by nitric acid to 3-fluoroanthraquinone-2-carboxylic acid, m. p. 183—185°, which loses carbon dioxide on heating and gives β-fluoroanthraquinone. 4-Fluoro-*m*-xylene yields a mixture of 5-*fluoro*-2 : 4-*dimethylbenzoyl*-o-*benzoic acid* (giving 4-*fluoro*-1 : 3-*dimethylanthraquinone*, m. p. 178°), and 3-*fluoro*-2 : 6-*dimethylbenzoyl*-o-*benzoic acid*, yellow needles, m. p. 126°, which gives no anthraquinone.

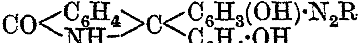
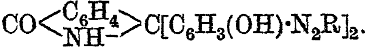
Iodobenzene and phthalic anhydride, with aluminium chloride in carbon disulphide, yield chiefly benzoyl-*o*-benzoic acid and iodine, but from the product by treatment with chlorine in chloroform solution p-*iodobenzoyl*-o-*benzoic acid chloride*, $C_{14}H_9O_3Cl_2I$, yellow granules, was obtained, melting with loss of chlorine without explosion. On treatment with chloroform, water, and sodium thiosulphate it yields p-*iodobenzoyl*-o-*benzoic acid*, m. p. 200° (*methyl* ester, m. p. 104—104·5°; *ethyl* ester, 81·5—82°; *propyl* ester, m. p. 52°; *butyl* ester, oil), and by solution in sodium hydroxide and acidification with hydrochloric acid is converted into p-*iodosobenzoyl*-o-*benzoic acid*, m. p. 179—180°. Treatment of *p*-iodobenzoyl-*o*-benzoic acid with sulphuric acid at 150—160° yields β-*iodoanthraquinone*, m. p. 175°. Phenyl methyl sulphide condenses with phthalic anhydride in the presence of aluminium chloride, yielding p-*methylthiolbenzoyl*-o-*benzoic acid*, fine, white needles, m. p. 154°, oxidised by chromic anhydride in acetic acid to p-*methylsulphonylbenzoyl*-o-*benzoic acid*, $SO_2Me\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CO_2H$, white flakes, m. p. 221°, condensing in sulphuric acid to anthraquinone-β-methylsulphone. Details are given for the determination of fluorine in organic compounds by fusion with sodium peroxide, calcium fluoride being precipitated and washed under standardised conditions. The following esters have been prepared: *methyl* p-*chlorobenzoyl*-o-*benzoate*, m. p. 110° (corresponding *ethyl* ester, m. p. 88°; *propyl* ester, m. p. 45°; *butyl* ester, oil); *methyl* p-*bromobenzoyl*-o-*benzoate* (*ethyl* ester, m. p. 83·5°; *propyl* ester, m. p. 51°; *butyl* ester, oil), and *methyl* m-*nitrobenzoyl*-o-*benzoate*, m. p. 100° (*ethyl* ester, m. p. 84°). R. B.

Sparassol. E. Wedekind and K. Fleischer (*Ber.*, 1924, **57**, [*B*], 1121—1123; cf. Wedekind and Fleischer, this vol., i, 174).—The authors agree with the conception of Pfau (this vol., i, 512) and Späth and Jeschki (*ibid.*, i, 513) that sparassol is methyl 4-hydroxy-6-methoxy-*o*-toluate.

4 : 6-Dimethoxy-*o*-toluic acid is remarkably stable towards alkaline permanganate, whereas 2 : 6-dimethoxy-*p*-toluic acid is readily oxidised to 2 : 6-*dimethoxyterephthalic acid*, m. p. 295°.

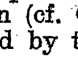
H. W.

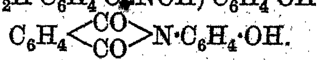
The Oximic and Iminic Compounds of Phenolphthalein. B. Oddo and D. Curti (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 354—357).—Previous results having shown that coupling with diazo salts serves as a means for determining the structure of the unstable phthaleins (A., 1913, i, 1110; 1916, i, 87), attention has now been directed to the oxime and imide of phenolphthalein. In presence of the amount of alkali hydroxide required by a molecule containing three replaceable hydrogen ions, treatment of the oxime with a diazo salt (1 or 3 mols.) results in the introduction into the molecule of only one azo group, whereas with the imide both mono- and bis-azo compounds are obtainable.

This difference in behaviour is explained on the assumption that, in so far as these coupling reactions are concerned, the oxime exhibits a quinonoid structure and thus gives the monoazo compound, $CO_2H{\cdot}C_6H_4{\cdot}C(:C_6H_4:NOH){\cdot}C_6H_3(OH){\cdot}N_2R$, whilst the imide is lactoid and thus yields the mono- and bis-azo compounds,

$CO<\substack{C_6H_4\\NH-}>C<\substack{C_6H_3(OH){\cdot}N_2R\\C_6H_4{\cdot}OH}$ and

$CO<\substack{C_6H_4\\NH-}>C[C_6H_3(OH){\cdot}N_2R]_2$.
In correspondence with these formulæ, the azo derivative of the oxime readily furnishes a diacetyl compound, whereas each of the imide derivatives yields a triacetyl compound.

When prepared in the ordinary way, phenolphthaleinoxime is always accompanied by the *p*-hydroxyphthalanil, obtained by Piutti by fusion of phthalic anhydride with *p*-aminophenol (A., 1886, 1026) and by Meyer by treating phenolphthaleinoxime, suspended in alcohol, with concentrated aqueous hydroxylamine hydrochloride solution (A., 1899, i, 707). The authors do not accept Meyer's explanation of the mechanism of formation of this phthalanil. Since phenolphthaleinoxime remains unaltered when treated with a faintly alkaline, absolute or 75% alcoholic solution of free hydroxylamine, the acid of the hydrochloride probably hydrolyses the oxime, giving *p*-hydroxybenzoyl-*o*-benzoic acid and β-phenylhydroxylamine:

$CO_2H{\cdot}C_6H_4{\cdot}C(C_6H_4{\cdot}OH):C_6H_4:NOH+H_2O \longrightarrow$

$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H+H_2:$  $:NOH \longrightarrow NHPh{\cdot}OH$.

The acid then yields the oxime, which undergoes isomerisation and loss of water, thus: $CO_2H{\cdot}C_6H_4{\cdot}C(:NOH){\cdot}C_6H_4{\cdot}OH \longrightarrow$ $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OH \longrightarrow$

$C_6H_4<\substack{CO\\CO}>N{\cdot}C_6H_4{\cdot}OH$.

The fact that only one azo group can be introduced into the molecule of dichlorophenolphthalein (cf. Consonno and Apostolo, A., 1921, i, 346) may be explained by the presence of the two chlorine atoms.

p-Hydroxyphthalanil forms pale yellow, lamellar crystals, m. p. 286°, and its *acetyl* derivative, white crystals, m. p. 235—236°. *Benzeneazophenolphthaleinoxime*, $C_{26}H_{19}O_4N_3$, forms dark green crystals, m. p. 202°, and its *diacetyl* compound, acicular crystals, m. p. 231—232°. *Benzeneazophenolphthaleinimide*, $C_{26}H_{19}O_3N_3$, forms minute, pale yellow crystals, m. p. 248—250°; its *triacetyl* derivative has m. p. 183°. *Bisbenzeneazophenolphthaleinimide*, $C_{32}H_{23}O_3N_5$, forms small, brownish-yellow crystals, m. p. 270—272°, and its *triacetyl* compound, brown, microscopic crystals, m. p. 207—208°.

T. H. P.

Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. V. Preparation of Primary Alcohols by the Catalytic Hydrogenation of Aldehydes. W. H. CAROTHERS and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, **46**, 1675—1683; cf. A., 1923, ii, 310).—The platinum oxide catalyst of Voorhees and Adams (A., 1922, ii, 558; cf. Adams and Shriner, A., 1923, ii, 773) has now been used for the reduction of a number of aldehydes, both aromatic and aliphatic. No promoter more powerful or satisfactory than ferrous chloride has been found, and the reductoins were carried out in the presence of 0·1 millimol. of ferrous chloride and 0·1725 g. of platinum oxide catalyst per 0·2 g.-mol. of aldehyde. Absorption of hydrogen is very slow in the absence of a solvent, and the most satisfactory general solvent is 95% ethyl alcohol. The effect of the solvent is to some extent specific, and solvents such as acetone or glacial acetic acid which give satisfactory results with benzaldehyde may give much slower reductions or undesirable secondary effects with other aldehydes. With technical methyl alcohol, benzaldehyde showed incomplete reduction (70%) owing to the formation of the dimethylacetal, but in the presence of 0·00034 mol. of sodium hydroxide or sodium methoxide the reduction was rapid and normal. The addition of alkali prevents acetal formation with the aliphatic aldehydes and also prevents the polymerisation of certain phenolic aldehydes which are very sensitive to traces of acid. The total reduction time may be decreased or increased by the addition of alkali, and the use of alkali is dependent on the specific case. By this method salicylaldehyde, vanillin, anisaldehyde, and piperonaldehyde give 92—96% of the theoretical yield of the corresponding alcohol in periods up to 1 hour, alkali being used in the first three cases. *p*-Chloro-, *p*-bromo-, and *o*-chloro-benzaldehyde are rapidly reduced to the corresponding alcohols in 92—96% of the theoretical yield, and the formation of appreciable amounts of halogen acid was not observed. Aldol gives an 86% yield of butan-1 : 3-diol in 2 hours, and in the same period butyraldehyde is completely reduced to the alcohol, the addition of alkali in the latter case (as with heptaldehyde) preventing acetal formation. With dextrose and other aldoses, the reduction by this method is too slow to be practicable. Resorcylaldehyde and *p*-dimethylaminobenzaldehyde were reduced readily, but only viscous products could be isolated. R. B.

Action of Nitroso Derivatives on Unsaturated Compounds. II. Synthesis of α-Ketodinitrones. L. ALESSANDRI (*Gazzetta*, 1924, **54**, 426—450; cf. A., 1915, i, 555; 1921, i, 730).—The action of nitrosobenzene on styrene is analogous to that on asarone the products being the *N*-phenyl derivative of benzaldoxime (phenyl-*N*-phenylnitrone), CHPh:NPh:O, azoxybenzene, formic acid, benzaldehyde, and benzoic acid. Miescher ("Nitrone and Nitrene," Dissertation, Zurich, 1918) found that nitrosobenzene and benzophenone hydrazone react to form the ketonitrone, diphenyl-*N*-phenylnitrone, and azoxybenzene. The author now finds that towards the *N*-phenyl ether of piperonaldoxime, which is an aldonitrone with the same $C{:}N$ grouping as this hydrazone but with the nitrogen quinquevalent and oxygenated, nitrosobenzene exhibits a more profound oxidising action, piperonaldehyde and azoxybenzene being formed in good yields.

In acetic acid solution, the action of ethyl *p*-nitrosobenzoate on tolane (cf. A., 1922, i, 558) results in the addition of this nitroso compound to the multiple linking of the tolane with formation of the *NN*-di-*p* : *p'*-carbethoxyphenyl ether of benzildioxime, $[CO_2Et{\cdot}C_6H_4{\cdot}NO{:}CPh{\cdot}]_2$, together with traces of benzoic acid and a small proportion of ethyl azoxybenzene-*p* : *p'*-dicarboxylate; the latter is also formed, together with benzil as principal product, and traces of benzoic acid, when the reaction occurs in chloroform solution. In this solvent, the action of nitrosobenzene on tolane yields the ketodinitrone, $(O{:}NPh{:}CPh{\cdot})_2$, the diversity in the behaviour of these two nitroso compounds being possibly dependent on the nature of the substituent in the para-position with respect to the nitroso group.

The action of nitrosobenzene on safrole yields the aldonitrone, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}NPh{:}O$, obtained by the condensation of piperonylacrolein with phenylhydroxylamine, together with azoxybenzene as secondary product. The interaction of ethyl *p*-nitrosobenzoate and safrole in ethereal solution gives ethyl azoxybenzene-*p* : *p'*-dicarboxylate and a small proportion of the *N*-*p*-carbethoxyphenyl ether of piperonylacroleinoxime.

The action of hydrazine sulphate on the *N*-phenyl ether of benzaldoxime yields benzaldazine and *p*-aminophenol.

The NN-*di*-p : p'-*carbethoxyphenyl ether* of *benzildioxime* (see above) forms masses of short, dull, sulphur-yellow crystals, m. p. 182—183° (decomp.) when heated rapidly, decomposing at about 178° when heated slowly, and resinifying rapidly in direct sunlight. When hydrolysed by means of dilute sulphuric acid in presence of alcohol, it yields benzil, ethyl azoxybenzene-*p* : *p'*-dicarboxylate, and the corresponding acid.

N-p-*Carbethoxyphenyl ether* of *piperonylacroleinoxime*,

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}NO{\cdot}C_6H_4{\cdot}CO_2Et,$$

forms short, orange crystals or minute needles, decomposing at 197—198°. N-p-*Carbethoxyphenyl ether* of *piperonaldoxime*,

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}NO{\cdot}C_6H_4{\cdot}CO_2Et,$$

prepared by the action of ethyl β-phenylhydroxylamine-*p*-carboxylate on piperonaldehyde, forms minute, flat, straw-yellow crystals, m. p. 145·5°. The last two compounds resinify rapidly with an odour of piperonaldehyde when exposed to direct sunlight.

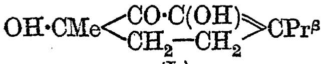
T. H. P.

Preparation of Phenylcarbamylhydrazones of *cyclo*-Hexenones. H. Mazourewitch (*Bull. Soc. chim.*, 1924, [iv], 35, 779—784).—The action of aniline on the semicarbazones and semicarbazidesemicarbazones of αβ-unsaturated cyclic ketones is analogous to that observed by Borsche (A., 1902, i, 486; 1904, i, 945; 1905, i, 305), ammonia being evolved with production of the phenylsemicarbazones (phenylcarbamylhydrazones). Mesityl oxide is an exception, the action of aniline on its semicarbazidesemicarbazone yielding hydrazodicarbonamide, $C_2H_6O_2N_4$, yellowish crystals, m. p. 228—230° (decomp.), and *s*-diphenylcarbamide, m. p. 234—236°. The semicarbazidesemicarbazone of 3-methyl-Δ^2-*cyclo*hexenone yields the *phenylsemicarbazone*, $C_{14}H_{17}ON_3$, yellowish needles, m. p. 173—174° (decomp.), the same product being obtained from the semicarbazone, together with a small quantity of a by-product, m. p. 195—198° (decomp.). The semicarbazidesemicarbazone and semicarbazone of 3 : 5-dimethyl-Δ^2-*cyclo*hexenone, yield 3 : 5-*dimethyl*-Δ^2-cyclo*hexenone phenylsemicarbazone*, $C_{15}H_{19}ON_3$, white needles, m. p. 191—192° (decomp.), together with, in the latter case, hydrazodicarbonamide, m. p. 233—234° (decomp.). Similarly, 3-methyl-5-ethyl-Δ^2-*cyclo*hexenone semicarbazone yields 3-*methyl*-5-*ethyl*-Δ^2-cyclo*hexenone phenylsemicarbazone*, m. p. 169—170°, the semicarbazidesemicarbazone yielding in addition *s*-diphenylcarbamide and an insoluble substance, m. p. 210—211° (decomp.). The semicarbazidesemicarbazone of 3-methyl-5-*iso*propyl-Δ^2-*cyclo*hexenone on warming with aniline yields 3-*methyl*-5-iso*propyl*-Δ^2-cyclo*hexenone phenylsemicarbazone*, m. p. 152—153° (decomp.), with an unidentified insoluble substance. R. B.

Constitution of Diosphenol [Buchu-camphor]. K. VON AUWERS (*Ber.*, 1924, 57, [*B*], 1106—1108).—Comparison of the spectroscopic constants of diosphenol with those of its methyl and ethyl ethers and acetate confirms the constitution assigned to it by Wallach (this vol., i, 156, 862) on purely chemical grounds. The following constants are recorded: Diosphenol, $d_4^{99\cdot2}$ 0·9524, $n_\alpha^{99\cdot8}$ 1·46079; $n_{\mathrm{He}}^{99\cdot8}$ 1·46473; $n_\beta^{99\cdot8}$ 1·47513. Diosphenol methyl ether, b. p. 240—242°/750 mm., 118—119°/10 mm., $d_4^{14\cdot2}$ 0·9930; $n_\alpha^{19\cdot2}$ 1·48405, $n_{\mathrm{He}}^{19\cdot2}$ 1·48783, $n_\beta^{19\cdot2}$ 1·49744, $n_\gamma^{19\cdot2}$ 1·50601, n_{He}^{20} 1·4852. Diosphenol ethyl ether, b. p. 242—246°/750 mm., 123—125°/10 mm., $d_4^{14\cdot0}$ 0·9825, d_4^{20} 0·977, $n_\alpha^{19\cdot0}$ 1·48405, $n_{\mathrm{He}}^{19\cdot0}$ 1·48788, $n_\beta^{19\cdot0}$ 1·49743, $n_\gamma^{19\cdot0}$ 1·50601, n_{He}^{20} 1·4852. Diosphenol acetate, b. p. 140—142°/12 mm., $d_4^{14\cdot6}$ 1·0415, d_4^{20} 1·036, $n_\alpha^{14\cdot6}$ 1·48027, $n_{\mathrm{He}}^{14\cdot6}$ 1·48378, $n_\beta^{14\cdot6}$ 1·49233, $n_\gamma^{14\cdot6}$ 1·49996, n_{He}^{20} 1·4814. H. W.

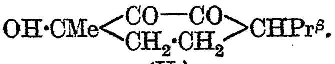
Catalytic Oxidation in presence of Platinum Black. Oxidation of Buchu-camphor. II. G. CUSMANO and E. CATTINI (*Gazzetta*, 1924, 54, 377—388).—The compound, $C_{10}H_{16}O_3$, obtained when an ethereal solution of buchu-camphor containing platinum black is left exposed to the air (A., 1923, i, 586), retains some of the properties of the buchu-camphor, and is converted into monobromobuchu-camphor (A., 1914, i, 303) when treated with hydrobromic acid. It is hence a hydroxybuchu-camphor, and since it is readily transformed by alkali hydroxide into two monobasic acids, $C_{10}H_{18}O_4$, which yield iodoform when treated with iodine and potassium hydroxide and consequently contain a methyl group joined to an alcoholic or carbonyl group, the hydroxyl group is situated at the carbon atom in the 1-position of the cymene skeleton.

Three tautomeric formulæ are admissible for buchu-camphor, and the solubility of hydroxybuchu-camphor and the fact that, like phenols, it gives a coloration with ferric chloride suggest for it structure (I), whereas its ability to react with two molecules of phenylhydrazine indicates for it also the tautomeric formula (II):



$\mathrm{OH{\cdot}CMe}<\begin{matrix}\mathrm{CO{\cdot}C(OH)}\\\mathrm{CH_2{-}CH_2}\end{matrix}>\mathrm{CPr^{\beta}}$

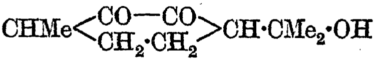
(I.)



$\mathrm{OH{\cdot}CMe}<\begin{matrix}\mathrm{CO{-}CO}\\\mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{CHPr^{\beta}}.$

(II.)

A hydroxybuchu-camphor of the structure



$\mathrm{CHMe}<\begin{matrix}\mathrm{CO{-}CO}\\\mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{CH{\cdot}CMe_2{\cdot}OH}$

could also, on hydrolysis, yield acids capable of giving the iodoform reaction, but that this occurs is excluded by the fact that monobromobuchu-camphor is readily convertible into 3-methyl-6-*iso*propylpyrocatechol. Moreover, one of the acids $C_{10}H_{18}O_4$ (III; cf. A., 1923, i, 586) obtained by hydrolysis of hydroxybuchu-camphor is formed also by the catalytic oxidation of buchu-camphor and is transformed, by oxidation and subsequent intramolecular condensation, into the acid, $\mathrm{CHMe_2{\cdot}CH}<\begin{matrix}\mathrm{CH_2{-}{-}CH_2}\\\mathrm{C(CO_2H){:}CH}\end{matrix}>\mathrm{CO}$ (cf. Semmler and Mackenzie, A., 1906, i, 373); the only such acid capable of undergoing this change has the formula

$\mathrm{OH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CHPr^{\beta}{\cdot}CO{\cdot}CO_2H}$.

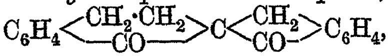
The other compound of the formula $C_{10}H_{18}O_4$ (cf. A., 1923, i, 586) is neutral, gives no coloration with ferric chloride, and is readily converted, by withdrawal of water, into hydroxybuchu-camphor. It appears to be the first product of the oxidation of buchu-camphor and to have the structure $\mathrm{OH{\cdot}CMe}<\begin{matrix}\mathrm{C(OH)_2{\cdot}CO}\\\mathrm{CH_2{-}CH_2}\end{matrix}>\mathrm{CHPr^{\beta}}$, being the hydrate of the diketonic form of hydroxybuchu-camphor; since the latter, in aqueous solution, shows the reactions of the enolic form, the failure of the reverse change is explainable.

The acid $\mathrm{OH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CHPr^{\beta}{\cdot}CO{\cdot}CO_2H}$ has m. p. 129°; its *sodium* salt forms long, transparent prisms containing water of crystallisation. The isomeric *acid*, also formed by the action of alkali on hydroxybuchu-camphor, forms crystals, m. p. 52°; its *barium* salt crystallises in long, silky needles, and when strongly heated, yields a liquid with the odour of mint. For this acid the tentative formula $\begin{matrix}\mathrm{CH_2{\cdot}CMe(OH)}\\|\\\mathrm{CH_2{-}{-}CHPr^{\beta}}\end{matrix}>\mathrm{C(OH){\cdot}CO_2H}$ is suggested.

T. H. P.

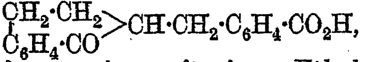
Spirans. XI. Preparation of Spirans with Five- and Seven-membered Rings. H. LEUCHS and F. REINHART (*Ber.*, 1924, 57, [*B*], 1208—1214).—*Ethyl* β-*phenylethylmalonate*, b. p. 185°/15 mm., is converted by benzyl chloride and sodium ethoxide into *ethyl benzyl*-β-*phenylethylmalonate*, b. p. 233°/12 mm., 237°/

16 mm., which is hydrolysed to *benzyl-β-phenylethylmalonic acid*, m. p. 153°. The acid is converted by the successive action of phosphorus pentachloride and ferric chloride into *hydrind-*1*-one-*1*-keto-*1 : 2 : 3 : 4*-tetrahydronaphthalene-*2 : 2*-spiran*,

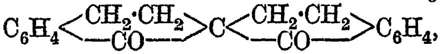
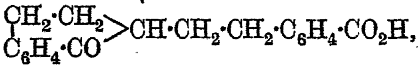


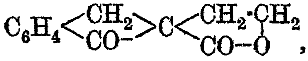
$$C_6H_4\lt\begin{matrix}CH_2\cdot CH_2\\ CO\end{matrix}\gt C\lt\begin{matrix}CH_2\\ CO\end{matrix}\gt C_6H_4,$$

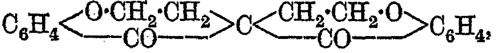
m. p. 111—112°, in which the presence of the ketonic group cannot be detected with phenylhydrazine or hydroxylamine. The spiran is converted by alcoholic sodium hydroxide solution into the *acid*



$$\begin{matrix}CH_2\cdot CH_2\\ |\\ C_6H_4\cdot CO\end{matrix}\gt CH\cdot CH_2\cdot C_6H_4\cdot CO_2H,$$

m. p. 113—115°, after previous softening. Ethyl di-β-phenylethylmalonate is hydrolysed to a mixture of di-β-phenylethylmalonic acid, m. p. 173—175° (decomp.) [Cohen and Marshall (T., 1915, **107**, 896) give m. p. 194—195°], and *ethyl hydrogen di-β-phenylethylmalonate*, m. p. 103° (the *ammonium* and *potassium* salts of the latter acid are described). Di-β-phenylethylmalonic acid is transformed by phosphorus pentachloride into the corresponding *chloride*, m. p. 83°, and thence into *di-*1*-keto-*1 : 2 : 3 : 4*-tetrahydronaphthalene-*2 : 2′*-spiran*,  $C_6H_4\lt\begin{matrix}CH_2\cdot CH_2\\ CO\end{matrix}\gt C\lt\begin{matrix}CH_2\cdot CH_2\\ CO\end{matrix}\gt C_6H_4$, m. p. 136—137°. Like the spiran described above, the compound is indifferent towards phenylhydrazine and hydroxylamine; it is converted by alcoholic sodium hydroxide solution into o-β-1-*keto-*1 : 2 : 3 : 4*-tetrahydronaphthylethylbenzoic acid*,  $\begin{matrix}CH_2\cdot CH_2\\ |\\ C_6H_4\cdot CO\end{matrix}\gt CH\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot CO_2H$, m. p. 161—162°.

Ethyl benzyl-β-phenoxyethylmalonate, b. p. 248°/16 mm., m. p. 53—54·5°, is converted successively into *benzyl-β-phenoxyethylmalonic acid*, m. p. 166—168° (decomp.); *benzyl-β-phenoxyethylmalonyl chloride*, m. p. 85—86°, and *benzyl-β-phenoxyethylmalonamide*, m. p. 170—171°. The chloride is decomposed by distillation under diminished pressure in the presence of ferric chloride into 1*-hydrindonebutyrolactone-*2*-α-spiran*,  $C_6H_4\lt\begin{matrix}CH_2\\ CO\end{matrix}\gt C\lt\begin{matrix}CH_2\cdot CH_2\\ CO-O\end{matrix}$, m. p. 110—111°, and a *substance*, (?) $C_{18}H_{12}O_2$, m. p. 176°. *Di-β-phenoxyethylmalonyl chloride*, m. p. 90° (corresponding *diamide*, m. p. 158—159°; *dianilide*, m. p. 187·5°), similarly suffers loss of phenol in a great measure when heated with ferric chloride, but yields small amounts of the *spiran*,



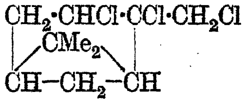
$$C_6H_4\lt\begin{matrix}O\cdot CH_2\cdot CH_2\\ CO\end{matrix}\gt C\lt\begin{matrix}CH_2\cdot CH_2\cdot O\\ CO\end{matrix}\gt C_6H_4,$$

m. p. 179—181°; *phenyl di-β-chloroethylmalonate*, m. p. 113—114°, is also obtained as a product of the action.

Di-β-phenoxyethylacetyl chloride has m. p. 82—83°, whilst the corresponding *amide* melts at 134—136°. H. W.

Cellulose Nitrate and Camphor. J. B. Nichols (*J. Physical Chem.*, 1924, **28**, 769—771).—Freezing-point determinations show that dry pyroxylin is rapidly peptised by camphor, and, to a slight extent, by monobromocamphor. Pyroxylin is decomposed by molten camphor. Mixtures of monobromocamphor and camphor exhibit a eutectic at 62·3°, containing 85·5% of the first-named constituent. S. K. T.

Dichloropinane and its Derivatives. M. Garino and A. D'Ambrosio (*Gazzetta*, 1924, **54**, 345—351).—For the compound $C_{10}H_{16}Cl_2$ obtained by Naudin (A., 1882, 608), the name dichloropinane is suggested, whereas Bert's dichloro compound (A., 1923, i, 812) is regarded as dichlorocamphane. Dichloropinane, which may be conveniently prepared by the action of sulphuryl chloride on pinene, is a pale yellow, neutral liquid, unstable in the light and having a persistent and pungent odour, d^{15} 1·1625, n_D^{20} 1·5008, $[\alpha]_D^{15}$ −20·175°. When distilled in a current of steam, it undergoes decomposition in accordance with the equation $3C_{10}H_{16}Cl_2 = C_{10}H_{16},HCl + C_{10}H_{15}Cl_3 + C_{10}H_{15}Cl + HCl$. Of these products, the first is pinene hydrochloride (bornyl chloride). The second, *trichloropinane* (annexed formula), is an unstable liquid, d^{15} 1·2550, n_D^{20} 1·5382, $[\alpha]_D^{15}$ −3·72°. The third *compound*, $C_{10}H_{15}Cl$, is a pale yellow liquid, b. p. 169—170° (decomp.), d^{15} 1·053, n_D^{20} 1·4980, $[\alpha]_D^{15}$ −11·52°.



The action of alcoholic ammonia solution on dichloropinane yields ammonium chloride and Marsh and Gardner's chlorocamphene (T., 1897, **91**, 288). T. H. P.

Formation of Borneol from Turpentine Oil. II. Y. Murayama, K. Abe, and S. Yamagishi (*J. Pharm. Soc. Japan*, 1924, No. 507, 341—347; cf. this vol., i, 62, and D.R.-P. 208487).—The effect of seven catalysts on the formation of borneol from an American turpentine oil, b. p. 158—161°, d^{15} 0·8644, $[\alpha]$ −6·00°, was studied. It was diluted with about twice its weight of carbon tetrachloride and warmed at 50°; a mixture of anhydrous oxalic acid and one of the following catalysts was added, stirring and keeping the temperature at 70—80°. Using aluminium, stannic, phosphoric, zinc and ferric chlorides, Japanese acid clay and wood charcoal as catalysts, the yields of borneol obtained were 22, 21, 0, 11·5, 25, 11, and 6·6% of the theoretical, respectively. When the oil was treated with oxalic acid only, the yield was 1·6%. K. K.

Kessyl Alcohol. I. Y. Sahina and G. Hongo (*J. Pharm. Soc. Japan*, 1924, No. 506, 227—238).—The physical and chemical properties of kessyl alcohol, $C_{14}H_{24}O_2$, m. p. 85°, obtained from *Valeriana officinalis*, L., var. *latifolia*, Miq., are identical with those described by Bertram and Gildemeister (A., 1891, 238) except $[\alpha]_D^{23}$ −44·72° in alcoholic solution. It gives a cherry-red coloration with a solution of vanillin in hydrochloric acid, contains no methoxy group, is stable towards potassium permanganate, does not absorb hydrogen in the presence of platinum, is not reduced by sodium and alcohol, and gives no iodoform reaction. It gives a *urethane*, $C_{21}H_{29}O_3N$, colourless plates, m. p. 168°; its *acetate* is a colourless, viscous liquid, b. p. 157—158°/6·5 mm. When oxidised with potassium dichromate and sulphuric acid, the alcohol gives an α-*ketone*, $C_{14}H_{22}O_2$, colourless needles, m. p. 105° (*semicarbazone*, m. p. 234—235°). With hydroxylamine in alkaline solution it gives two *oximes*, $C_{14}H_{23}O_2N$, m. p. 153—154° and 42° [or $(+\frac{1}{2}H_2O)$ m. p. 65—69°]. When treated with cold concentrated sulphuric acid, the oxime, m. p. 153—154°, gives a yellow powder, m. p. 160°, whereas with warm concentrated sulphuric acid it forms a yellow powder, $C_{14}H_{21}ON$, m. p. 155°. The α-ketone is converted by boiling alcoholic hydrogen chloride into a β-isomeride, white needles, m. p. 111—112°, which gives no coloration with vanillin–hydrochloric acid; the *semicarbazone* has m. p. 190—191°. The α-ketone is reduced by sodium and alcohol to iso*kessyl alcohol*, white prisms, m. p. 118—119° (*phenylurethane*, m. p. 50—52°). Ethyl nitrite and sodium in an ethereal solution convert the α-ketone into the *compound*, $C_{14}H_{23}O_4N$, m. p. 100—108° (copper salt, m. p. 168—169°). From these results, the authors conclude that kessyl alcohol is a saturated secondary alcohol having two benzene rings and an ethereal oxygen atom. K. K.

Constitution of Caoutchouc. VI. H. Staudinger (*Ber.*, 1924, **57**, [*B*], 1203—1208).—Harries's conception that fully reduced caoutchouc would be molecular-disperse and capable of distillation under diminished pressure without decomposition is not in harmony with the observation that hydrocaoutchouc is colloidal and is decomposed at 350—400° into a series of ethylenic hydrocarbons of which the most complex has (approximately) the composition $C_{50}H_{100}$, whereas the simplest is β-methyl-Δ^{α}-butene (identified by oxidation to methyl ethyl ketone and preparation of the *p*-nitrophenylhydrazone of the latter). The hypothesis that β-methyl-Δ^{α}-butene is the unit of hydrocaoutchouc whereas caoutchouc is derived from isoprene is in accord with the observation that hydrocaoutchouc is completely decomposed at 350—400° whereas caoutchouc requires only a temperature of 300—350°, since the substituents are usually loosely united in allyl derivatives. It is considered that caoutchouc is a derivative of ethylene of very high molecular weight in which a large number of isoprene molecules are similarly united chemically. These molecules are considered to be identical with the colloidal particles; they are not uniform and probably have very varying magnitudes which alter with changing temperature. The term "macromolecule" is proposed for this particular type. This conception of the constitution of caoutchouc is in contradiction to the properties of hydrocaoutchouc obtained by Pummerer and Burkard (A., 1923, i, 49) particularly with respect to the autoxidisability of the substance to *iso*caoutchouc. Attempts to repeat the experiments of these chemists with a less completely purified specimen of caoutchouc failed to give a completely hydrogenated product at the atmospheric pressure. At 100°, however, hydrocaoutchouc was readily prepared which was identical in all respects with the product obtained previously at 270° under high pressure in the presence of platinum or palladium. It does not suffer autoxidation. The action of zinc methyl or zinc ethyl on bromohydrocaoutchouc gives *methyl-* and *ethyl-hydrocaoutchoucs* which behave like paraffinoid hydrocarbons of high molecular weight. H. W.

Resinic Nature of Shellac. Attempts to Effect a Partial Synthesis. C. Harries and W. Nagel (*Wiss. Veröff. Siemens-Konz.*, 1924, **3**, 12—18).—By heating aleuritic and shellolic acids (A., 1923, i, 120) together in various molecular proportions under reduced pressure for 1 hour at 150—160°, lactide condensation takes place with vigorous evolution of water vapour, and clear yellow liquids are obtained which solidify on cooling to yellow, resinous masses. These products are readily soluble in most organic solvents, have low melting points, and are readily hydrolysed by alkali hydroxides, giving salts of the original acids. If the heating is continued above 200° the substances swell suddenly and are converted into harder, more infusible resins which, however, are decomposed by potassium hydroxide with the formation of potassium salts of the original acids. Aleuritic acid alone is converted at 170° into a white, opaque mass, m. p. 35—45°; shellolic acid alone gives a yellow, very brittle, resin at 202—210°, which is soluble in chloroform, and on further heating decomposes with the evolution of carbon dioxide. Similar results were obtained when the amorphous acids of ordinary shellac were heated under the above conditions. It appears therefore that shellac is a mixture of products obtained by the lactide condensation of various hydroxycarboxylic acids. A. R. P.

Amygdalin. III. *l*-Amygdalinic Acid. G. Zemplén and A. Kunz (*Ber.*, 1924, **57**, [*B*], 1194—1200).—Amydalin is converted by hydrolysis with barium hydroxide and acetylation of the barium salts thus produced by acetic anhydride in the presence of pyridine into a mixture of the hepta-acetyl derivatives of *d*- and *l*-amygdalinic acids which has $[\alpha]_D^{16}$ +36·1° in chloroform. Solution of the mixture in warm anhydrous benzene followed by addition of ether causes the separation of *labile* l-*hepta-acetylamygdalinic acid*, m. p. 115° (indefinite), $[\alpha]_D^{18}$ +60·06°, in long needles which cannot be recrystallised from any solvent. It is hydrolysed to *l*-amygdalinic acid, $[\alpha]_D^{18}$ —132·7° in aqueous solution and yields *l*-mandelic acid, $[\alpha]_D^{18}$ —144° in water. Hydrolysis of the mixture of acids having $[\alpha]_D^{16}$ +36·1° in chloroform (see above) followed by re-acetylation gives a product which has $[\alpha]_D^{18}$ —8·4° in chloroform, from which *stable* l-*hepta-acetylamygdalinic acid*, needles, m. p. 195—196°, $[\alpha]_D^{18}$ —65·5° in chloroform, is isolated by repeated crystallisation from absolute alcohol. It yields *l*-mandelic acid, $[\alpha]_D^{18}$ —153·4° in water, and *l*-amygdalinic acid, $[\alpha]_D^{18}$ —133·2° in aqueous solution. Labile can be transformed into stable *l*-hepta-acetylamygdalinic acid by hydrolysis with absolute methyl-alcoholic sodium methoxide solution followed by re-acetylation with acetic anhydride in the presence of pyridine. The nature of the isomerism is not explained. H. W.

Seneginin [Seneginic Acid], the Ultimate Sapogenin from *Radix Senegæ*. E. WEDEKIND and R. KRECKE (*Ber.*, 1924, **57**, [*B*], 1118—1120).—Crude senegin is boiled with sulphuric acid (5%) and the undissolved portion is treated with perchloric acid (3%) at 140° until further production of sugar is not observed. The product, which is designated *seneginin* or *seneginic acid*, $C_{26}H_{44}O_6$, forms colourless needles, m. p. about 272°, $[\alpha]_D$ +38·26° in alcoholic solution. The formation of a *diacetate*, m. p. 214° after previous softening, and of a *dimethyl* ester, m. p. 206—208°, $[\alpha]_D$ +32·09° in methyl-alcoholic solution, shows it to be a dibasic dihydroxy-acid. H. W.

Orobanchin, a New Glucoside, extracted from Roots of *Orobanche rapum*, Thuill. M. BRIDEL and C. CHARAUX (*Compt. rend.*, 1924, **178**, 1839—1842).—Fresh roots of *O. rapum* were treated with boiling 95% alcohol and the extract was concentrated until crystals were obtained. Purification of these yielded *orobanchin*, prismatic crystals, m. p. 160°, α_D −66·22°. The crystals lose 10·73% of their weight when kept in a vacuum at 50°; the value of α_D for the dry product is −74·18°. The glucoside has reducing properties, 1·0 g. being equivalent to 0·120 g. of dextrose. Hydrolysis at 105° by 3% sulphuric acid resulted in the formation of rhamnose, dextrose, and caffeic acid, together with other products not yet identified. H. J. E.

Hydroxymethylfurfuraldehyde. J. A. MIDDENDORP (*Z. Ver. deut. Zuckerind.*, 1924, **814**, 338—433).—A German translation of the paper in *Rec. trav. chim.*, 1919, **38**, 1—71 (see A., 1919, i, 129). F. A. M.

Elsholtzia Ketone (Elsholtzione). Y. ASAHINA [with Y. MURAYAMA, B. SHIBATA, T. KARIYONE, S. KUWADA, and M. ASANO] (*Acta Phytochim.*, 1924, **2**, 1—23; cf. A., 1915, i, 429; 1920, i, 495; 1922, i, 1047).—A review of previous work on the constitution of elsholtzione and of elsholtzic acid, the following additional evidence being given in support of the previously assigned formulæ. Crude elsholtzione is best purified by boiling the fraction of b. p. 210—220°, 95—110°/15 mm., with hydroxylamine hydrochloride and sodium acetate in absolute alcohol for 2—3 hours: the oxime thus obtained is then hydrolysed by boiling with 5% hydrochloric acid. The pure ketone (b. p. 92°/9 mm.) when treated in dry ethereal solution with amyl nitrite and sodium, affords *ethyl elsholtzate*, colourless leaflets, m. p. 49°, b. p. 205°, and *iso*butylaldoxime. Elsholtzic acid, the preparation of which has been described, gives a *sodium* salt (+1H_2O) and a *potassium* salt, both colourless crystals, *calcium*, *barium*, and *silver* salts, anhydrous and colourless, *lead* salt (+1H_2O), white leaflets, *cupric* salt (+6H_2O), green leaflets, *ferric* salt, $[(C_6H_5O_3)_2Fe]_2O,9H_2O$, yellow needles, *methyl* ester, colourless leaflets, m. p. 36—38°, *chloride*, needles, m. p. 21—22°, *amide*, m. p. 85—86°, and an *anilide*, m. p. 91°.

Furan-α-carboxylic acid, when treated with Caro's acid, gives carbon dioxide, and fumaric, maleic, and succinic acids. Elsholtzic acid, when similarly treated, gives carbon dioxide and an oily product which, after being distilled in steam and then reduced with hydrogen and platinum black, gives methylsuccinic acid. Ethyl elsholtzate, when treated with ethyl acetate and sodium, gives *ethyl elsholtzoylacetate*, $C_4H_2O(Me)\cdot CO\cdot CH_2\cdot CO_2Et$, a viscous, yellow oil of unpleasant odour, b. p. 145—150°/15 mm., d_4^{17} 1·1437, n_D^{19} 1·50044. This ester, when heated with hydroxylamine hydrochloride and 20% sodium hydroxide solution, gives no oxime, but a *substance*, $C_8H_7O_3N$, colourless needles, m. p. 95°, which is probably an *iso*oxazolone derivative. When elsholtzoyl chloride is treated at 190—200° in direct sunlight with 2 mols. of bromine, the product, after decomposition with water, yields 3-*aldehydofuran*-2-*carboxylic acid*, colourless needles, m. p. 158°, *phenylhydrazone*, yellow needles, sintering at 166°, m. p. 171° (decomp.). The aldehydo-acid, when treated with hydroxylamine hydrochloride and sodium acetate, gives an *oxime*, m. p. 225°, but when digested with alcoholic hydroxylamine hydrochloride gives a *substance*, softening at 105°, m. p. 211°, which has no constant composition, and is probably an oxime anhydride. The oxime, when heated with acetic anhydride, gives 3-*cyanofuran*-2-*carboxylic acid*, white needles, m. p. 183°; the latter when oxidised with ammoniacal silver oxide solution gives furan-2 : 3-dicarboxylic acid (methyl ester, m. p. 37°; cf. A., 1922, i, 1047). 2-Methylfuran-3-carboxylic acid (preparation from ethyl acetoacetate, A., 1911, i, 319) gives a *chloride*, fuming liquid, b. p. 68—70·5°/14 mm., colourless when pure; if this chloride is treated at 120—140° in direct sunlight with bromine, the product, after decomposition with water and treatment in succession with silver oxide and with zinc and ammonium chloride, gives furan-2 : 3-dicarboxylic acid, prisms by sublimation, m. p. 221°. The acid and its methyl ester are identical with the similar acid and ester obtained from elsholtzic acid.

[With M. TANAKA.]—Elsholtzic acid, when heated at 210—230° in a closed tube, gives 3-*methylfuran*, a colourless liquid, b. p. 65·5°, d_4^{18} 0·923, n_D^{18} 1·4255.

The colours developed by many furan derivatives with vanillin solution are tabulated: they are mostly red or reddish-violet. 3-Methylfuran gives a bluish-green pine-shaving reaction.

F. G. M.

Thioindigo and its Derivatives. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (O. SPENGLER and A. THURM) (D.R.-P. 386889; from *Chem. Zentr.*, 1924, i, 1449).—The following compounds, obtained from the halogenation of ω-disulphides of arylmethylketones and condensation of the resulting products, are mentioned: *di(benzoylmethyl) disulphide*, m. p. 75—76°; *di*-(4-*methylbenzoylmethyl*) *disulphide*, m. p. 85·5—86·5°; 6 : 6′-*dimethyl*-

thioindigo; *di-(3 : 4-dichlorobenzoylmethyl) disulphide*, colourless leaflets, m. p. 89—90°. G. W. R.

Synthesis of Ephedrine. E. Fourneau and S. Kanao (*Bull. Soc. chim.*, 1924, [iv], **35**, 614—625).—A critical survey of the published researches on the constitution and synthesis of ephedrine, for details of which the original should be consulted. A comprehensive bibliography is appended. The base obtained by reducing, with sodium amalgam, the product of the action of methylamine on brominated benzyl methyl ketone (cf. Emde, A., 1906, i, 945; 1909, i, 708; 1910, i, 479; 1911, i, 714) is identical with that obtained starting from propenylbenzene (Fourneau and Puyal, A., 1923, i, 238). The action of methylamine on brominated phenyl ethyl ketone is much slower than in the preceding case, and the base obtained on reducing the product is identical with ψ-ephedrine, whilst racemic ephedrine itself appears to have been first obtained by Eberhard (A., 1915, i, 834; 1917, i, 392; 1920, i, 875) by carrying out the reduction with hydrogen in presence of palladium.

F. G. W.

Actinine. D. Ackermann, F. Holtz, and H. Reinwein (*Z. Biol.*, 1924, **81**, 61—64; cf. A., 1923, i, 1155; this vol., i, 243).—There is doubt whether the formula of the base "actinine," isolated from a species of sea-anemone by the authors, is $C_{13}H_{24}O_5N_2$ or $C_7H_{13}O_2N$. The latter is the formula of stachydrine, hitherto found only in plants. The discovery of trigonelline in an animal and the frequent occurrence of glycine-betaine makes it quite probable that stachydrine, which is also a betaine, should occur in the animal world. From a comparison of the composition, m. p., and other properties of actinine chloroaurate, chloroplatinate, and of the compounds obtained with potassium ferro- and ferri-cyanides with those of similar compounds of stachydrine, it is considered that actinine is identical with stachydrine, although the evidence is not conclusive.

C. T. G.

Supposed Calcium–Nicotine Compounds. R. W. Thatcher.—(See ii, 635.)

Amination of Nicotine with Sodamide and Potassamide. A. E. Tschitschibabin and A. W. Kirssanow (*Ber.*, 1924, **57**, [*B*], 1163—1168).—In a previous communication (Tschitschibabin and Buchholz, A., 1923, i, 594) the formation of one of the two possible 2-aminonicotines (m. p. 124—125°) has been described. It is now found that both isomerides are produced in approximately equal amounts when nicotine dissolved in xylene is heated with sodamide at 135—140°. They are most readily separated from one another by taking advantage of the ready solubility of 6-amino-3-methylpyrrylpyridine in water, in which 2-amino-3-methylpyrrylpyridine (m. p. 124—125°) is very sparingly soluble. *6-Amino-3-methylpyrrylpyridine* has m. p. 60°, b. p. 300° (slight decomp.), or 167°/12 mm. The *hydrochloride*, *chloroplatinate* (+H_2O), *nitrate*, *sulphate*, and *picrate*, m. p. 225° (decomp.), are described. The *hydrochloride*, *nitrate*, and *sulphate* of 2-amino-

3-methylpyrrylpyridine have been prepared. Treatment of the aminonicotines dissolved in dilute sulphuric acid with bromine yields, respectively, *5-bromo-2-amino-3-methylpyrrylpyridine*, m. p. 138—138·5°, and *5-bromo-6-amino-3-methylpyrrylpyridine*, m. p. 111—112°. 6-Amino-3-methylpyrrylpyridine hydrochloride dissolved in sulphuric acid (5%) is converted by sodium nitrite into *6-hydroxy-3-methylpyrrylpyridine*, m. p. 103·5—104°. The amines dissolved in saturated hydrochloric acid solution are slowly converted by sodium nitrite at 20—30° into the corresponding chloronicotines; *2-chloro-3-methylpyrrylpyridine* has b. p. 268—269°/740 mm., d_4^{20} 1·1378, d_4^0 1·1520, n_D^{15} 1·5457, whereas *6-chloro-3-methylpyrrylpyridine* has b. p. 270—271°/742 mm., d_4^{20} 1·100, d_4^0 1·1162, n_D^{20} 1·5485. Oxidation of the chloro compounds with potassium permanganate gives 2-chloropyridine-3-carboxylic acid, m. p. 193°, and 6-chloropyridine-3-carboxylic acid, m. p. 199°, respectively.

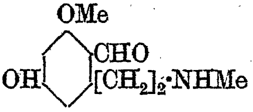
The aminonicotines and their salts are optically inactive, so that their production is accompanied by racemisation. The physiological action of the amino- and 6-hydroxy-nicotines is similar to, but markedly less toxic than, that of nicotine. H. W.

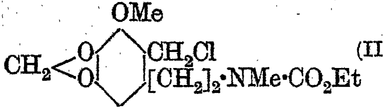
Change of Cotarnine and its Derivatives by Ladenburg's Reduction. H. KONDO and T. NAKAZATO (*J. Pharm. Soc. Japan*, 1924, No. 507, 326—341).—By reducing hydrocotarnine with sodium and amyl alcohol, Pyman and Remfry (T., 1912, **101**, 1595) obtained hydrohydrastinine and a small amount of a mixture of four phenolic bases. Applying the method to cotarnine, the authors have isolated hydrohydrastinine, a white, crystalline powder, m. p. 268°, and a phenolic base (I), m. p. 199°, identical with Pyman's 6-hydroxy-8-methoxy-2-methyltetrahydro*iso*quinoline; the *hydrobromide* of its benzoyl derivative melts at 226—228°. The yields of the former free base and of (I) were 20% and 10% of the material used, respectively. Pyman's three other bases have not been isolated. By heating (I) with concentrated hydrochloric acid in a sealed tube, the *dihydroxy* compound, $C_9H_9NMe(OH)_2$, m. p. 220°, resulted, which gave a brown coloration with ferric chloride. When oxidised with iodine in alcoholic solution, hydrocotarnine gave *cotarnine hydriodide di-iodide*,

$$C_{12}H_{15}O_4N,HI,I_2,$$

m. p. 144°. By the same method, (I) gave the *hydriodide* of an aldehydo-base, $C_{11}H_{15}O_3N,HI$, needles, m. p. 202°. The free *base*, $C_{11}H_{15}O_3N$, colourless prisms, m. p. 146°, has the formula (II).

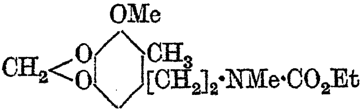
(II.)

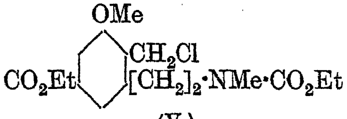




(III.)

It reduces ammoniacal silver nitrate solution, but not Fehling's solution; the *semicarbazone* melts at 208°. The base (I) does not react with acetic anhydride or benzoyl chloride, but is converted by benzoic anhydride into a *monobenzoyl* derivative (*hydrobromide*, $C_{18}H_{19}O_3N,HBr$, yellow prisms, m. p. 226—228°). The nucleus of (I) cannot be split by heating with benzoic anhydride in a sealed tube. When a mixture of anhydrous hydrocotarnine and ethyl chloroformate was heated for 2 hours, a *substance* (III), colourless prisms, m. p. 122°, was obtained. By reducing (III) with 3%


(IV.)


(V.)

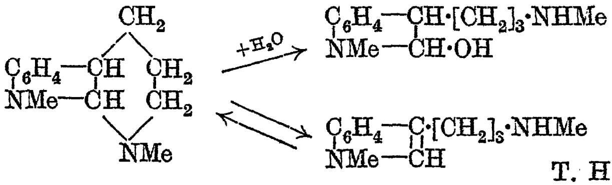
sodium amalgam in alcoholic solution at room temperature, *substance* (IV), $C_{15}H_{21}O_5N$, was obtained as colourless prisms, m. p. 62°. This was not affected by further treatment, in boiling alcohol, with sodium amalgam. If (III) is reduced with a large excess of sodium amalgam in boiling alcohol, hydrocotarnine is produced as the main product and is accompanied by a small amount of (IV). On heating (I) with ethyl chloroformate, a brown, amorphous *substance* (V), $C_{17}H_{24}O_6NCl$, m. p. 132—139°, was obtained. K. K.

Fluorescence of the Alkaloids of the *iso*Quinoline and Tetrahydro*iso*quinoline Group: Papaverine, Narcotine, Hydrastine, and their Decomposition Products. E. Bayle and R. Fabre (*Compt. rend.*, 1924, **178**, 2181—2183).—The colour and intensity of the fluorescence of the alkaloids excited by the mercury line 3650 (taking the intensity of sodium salicylate as 20) is as follows: Papaverine, whitish-blue, 6; hydrastine, greenish-white, 55; narcotine, very faintly violet, not measurable; narceine, bluish-violet, 7; veratric acid, bluish-white, 5; opianic acid, bluish-white, 10; potassium opianate, blue, 5; hydrastinine and cotarnine, nil; hydrastine hydrochloride, blue, 36; hydrastinine hydrochloride, 4; cotarnine hydrochloride, yellow, 35. A. Cousen.

Tautomerism of Eserine. M. and M. Polonovski (*Compt. rend.*, 1924, **179**, 57—60).—Further results confirm the view that eseretholemethine is a pseudo-base with an aldolic hydroxyl (cf. *ibid.*, **178**, 2078), the action of sodium on the base in ethereal solution yielding a voluminous, amorphous precipitate of the sodium salt, which is decomposed by water into sodium hydroxide and the original methine. The ethoxide is converted by hydrochloric acid quantitatively into eserethole methochloride, and, when treated with methyl iodide (2 mols.) in absolute alcohol yields the dimethiodide, m. p. 207° (A., 1923, i, 939).

The action of hydrogen cyanide on eseretholemethine gives the basic *cyanoeseretholemethine* (3-β-*dimethylaminoethyl*-2-*cyano*-1-*methyl*-2:3-*dihydroindole*), a colourless oil, $[\alpha]_D$ −10°, forming a *methiodide*, $C_{16}H_{23}ON_2{\cdot}CN,MeI$.

It appears likely that eserine can react, besides, as the ordinary tertiary basic, tricyclic form, also as a secondary, open-chain base, either hydrated (eserinol) or anhydrous (eserinamine), the latter being tautomeric with eserine :



T. H. P.

Physostigmine (Eserine). II. Synthesis of Physostigmol Ethyl Ether. E. Stedman (*J. Chem. Soc.*, 1924, **125**, 1373—1376).—When eserethole methiodide is heated under greatly reduced pressure, it fuses and physostigmol ethyl ether sublimes slowly therefrom. It was not found possible to investigate the latter substance by a process of degradation, but an indication was given that physostigmol is 5-hydroxy-1 : 3-dimethylindole. By Kermack, Perkin, and Robinson's method (*ibid.*, 1921, **119**, 1622), methyl-*p*-phenetidine was converted first into nitrosomethyl-*p*-phenetidine, which was reduced to *p*-ethoxyphenylmethylhydrazine. This was condensed with α-ketoglutaric acid and the product heated to drive off carbon dioxide, whereby 5-ethoxy-1 : 3-dimethylindole was obtained, identical with physostigmol ethyl ether. The synthesis serves to locate the position of the hydroxyl group in eseroline. A. Cousen.

Alkaloids of Yohimbehe Bark. P. W. Danckwortt and P. Luy (*Arch. Pharm.*, 1924, **262**, 81—104).—The residues from the technical extraction of yohimbine contain, besides unseparated yohimbine, a phenol-like constituent and another *alkaloid*, $C_{20}H_{24}O_3N_2$ (?), m. p. 133—135° (with previous darkening), $[\alpha]_D$ +122·32° in alcohol. This substance is isolated as an amorphous mass, neither it nor any derivative being ever obtained in a crystalline state. The following salts are all pale yellow substances, darkening before they melt or decompose: *hydrochloride*, m. p. 215—216° (this salt is soluble in acetone and on this property the separation from yohimbine was based, the alkaloid mixture being originally extracted as oxalate); *nitrate*, m. p. 185°; *acetate*, m. p. 155—156°; *oxalate*, m. p. 215° (decomp.); *sulphate*, decomp. 120°; *picrate*, decomp. 140—145°; *picrolonate*, decomp. 145—150°. A *chloroaurate* and a *chloroplatinate* are described, but neither contains the expected percentage of metal. A (mono) *acetyl* derivative having m. p. 102—103°, and, like yohimbine (cf. Barger and Field, T., 1915, **107**, 1025), a sulphonic acid (not crystalline), m. p. 293—298° (decomp.), are formed. When treated with methyl iodide in ether solution, the substance gives what appears to be a mixture of *mono-* and *di-methiodides*, whilst this with more methyl iodide at 125° yields apparently a dimethiodide of a di-iodo derivative. About 75% of the calculated amount of methyl iodide, assuming one methoxyl group to be present, was obtained by Zeisel's method. The substance seems to contain no carbonyl or methylenedihydroxy groups, and the presence of an *N*-methyl group, although indicated, was not proved quantitatively. A *dihydro* derivative, m. p. 115°, is obtained by reduction with sodium amalgam. Yohimbine by similar treatment is also reduced, but to what stage is not certain (the *product* has m. p. 215—215·5°), whilst if the reduction be carried out with Devarda's alloy in alkaline alcoholic solution an intensely coloured *substance*, m. p. about 210—220°, is obtained. Yohimbine is decomposed by the action of hydrochloric acid at 100°, a *compound*, m. p. about 270°, apparently not yohimboaic acid (Spiegel, A., 1903, i, 274), being formed. The new alkaloid is decomposed by hot alcoholic sodium hydroxide and affords an *acid*, m. p. 151—153°, presumably analogous to yohimboaic acid (*loc. cit.*). When treated with "bromide–bromate" solution, yohimbine takes up 3·4 atomic proportions of bromine, whilst with iodine 3 atomic proportions are taken up and the product is periodide-like in nature. The new base may possibly be identical with the yohimbenine described by Spiegel (A., 1899, i, 966; 1903, i, 195).

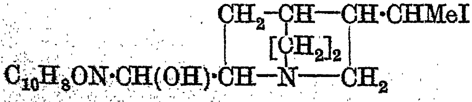
W. A. S.

Hydriodoquinine and its Transformation Products. K. W. Rosenmund and C. Kittler (*Arch. Pharm.*, 1924, **262**, 18—24).—Hydriodoquinine, isolated as the dihydriodide $C_{20}H_{27}O_2N_2I_3$, pale yellow crystals discoloured at 215°, decomp. 235° (cf. Lippmann and Fleissner, A., 1891, 1517; Skraup, A., 1892, 83; 1893, i, 737) is a mixture of two substances. The base, $C_{20}H_{25}O_2N_2I$, was separated into two distinct crops of crystals, mixed crystals also being formed. *Base* I forms clusters of needles, $[\alpha]_D$ −74·3°; *dihydrochloride*, pale yellow prisms; *base* II, felted, opaque needles more soluble in benzene and less soluble in ether than I, $[\alpha]_D$ −128·3°; *dihydrochloride*, bright yellow needles. On heating, both I and II become yellow at 105—110°, blacken at 120—130°, and decompose at 140—150°.

Base I, treated for several days with alcoholic sodium hydroxide and a little copper acetate, yields pseudoquinine, m. p. 186°. Prolonged heating with cuprous cyanide in benzene solution converts I into *hydrocyanoquinine*, $C_{21}H_{15}O_2N_3$, m. p. 175°, whilst reduction by means of hydrogen with a catalyst in neutral alcoholic solution gives dihydroquinine, $C_{20}H_{26}O_2N_2$, m. p. 168°, identical with the product of hydrogenation of pseudoquinine.

Base II, when treated with alcoholic sodium hydroxide, cuprous cyanide, or hydrogen in the same way, yields in each case niquine, m. p. 146° (Skraup, A., 1893, i, 56), for which the formula $C_{20}H_{24}O_2N_2$ is preferred to that adopted by Skraup, $C_{19}H_{24}O_2N_2$, since these three mild reactions are not likely to have caused loss of an atom of carbon. In the last two reactions there were also formed *substances* of m. p. 85—95° (decomp.) and 92—93°, respectively.

Base I has the true hydriodoquinine structure, the iodine atom probably occupying the α-position in the side chain as in the annexed formula; but in base II the bridge in the quinuclidine nucleus has probably already been ruptured as suggested by Léger in the case of niquine (A., 1919, i, 597).



$$\begin{array}{l} \quad CH_2-CH-CH\cdot CHMeI \\ \quad\;\; | \qquad [CH_2]_2 \;\; | \\ C_{10}H_8ON\cdot CH(OH)\cdot CH-N-CH_2 \end{array}$$

G. M. B.

Strychnos Alkaloids. XLII. Action of Halogen on Cacotheline and Related Substances. H. LEUCHS and C. TAUBE (*Ber.*, 1924, 57, [*B*], 1092—1098).—The final product of the action of bromine on cacotheline is the hydrobromide of an acid, $C_{19}H_{22}O_6N_2$ (cf. Hanssen, *Ber.*, 1897, **20**, 452). The intermediate products of the change have now been investigated. It appears probable that Hanssen's compound is a γ-aldehydo- or an α-keto-acid, although the reactions characteristic of these groups have not been observed with it.

Cacotheline is converted by treatment with bromine in aqueous solution at 20° into the *substance*, $C_{21}H_{23}O_8N_3Br_2$, which liberates iodine from potassium iodide and evolves bromopicrin when boiled with water. It is reduced by sulphur dioxide to the *salt*,

$$C_{21}H_{23}O_8N_3,HBr,6H_2O,$$

which, when dried or crystallised from *N*-hydrobromic acid, readily loses carbon dioxide and yields the *compound*, $C_{20}H_{23}O_6N_3,HBr$. The free *acid*, $C_{20}H_{23}O_6N_3$, its *hydrochloride* and *nitrate* are described. Methylcacotheline and bromine yield the *substance*,

$$C_{22}H_{26}O_8N_3Br_3,3H_2O,$$

yellow prisms, which is reduced by sulphur dioxide under certain conditions mainly to the *product*, $C_{22}H_{26}O_8N_3Br$, which readily loses carbon dioxide when dried or treated with warm water and yields the *compound*, $C_{21}H_{26}O_6N_3Br$.

The product of the action of bromine on the nitroquinone hydrate of brucinesulphonic acid is shown to be reduced by sulphur dioxide to a substance, $C_{20}H_{23}O_9N_3S$, whilst the corresponding amine hydrochloride has the composition, $C_{20}H_{23}O_6N_3S,HCl,3H_2O$; the free *amine*, $C_{20}H_{23}O_6N_3S$, is described. Bromine transforms the compound, $C_{20}H_{23}O_9N_3S$ into the *substance*, $C_{20}H_{23}O_{10}N_3SBr_2$ or $C_{20}H_{25}O_{10}N_3SBr_2$.

Cacotheline is converted by chlorine at 0° into the *compound*, $C_{21}H_{23}O_8N_3Cl_2$, which is transformed by 3*N*-nitric acid into the *substance*, $C_{21}H_{23}O_8N_3Cl_2,HNO_3$. Similarly, methylcacotheline yields the *substance*, $C_{22}H_{25}O_8N_3Cl_2,5H_2O$, which is also obtained in the anhydrous condition. The products do not appear to be similar to those yielded by bromine under analogous conditions. H. W.

Attempts to Prepare 2-Methoxy-1-methylpiperidine. Hydrogenation of certain Pyridine Derivatives. T. B. GRAVE (*J. Amer. Chem. Soc.*, 1924, **46**, 1460—1470).—Reduction of 2-methoxypyridine, with sodium and alcohol, electrolytically in dilute sulphuric acid, or with hydrogen in acetic or hydrochloric acid, or methyl alcohol, in presence of platinum, yields piperidine. 2-Methoxymethylpyridinium sulphate yields 1-methylpiperidine when treated with hydrogen in methyl alcohol in presence of platinum black, whilst 2-chloropyridine yields similarly a mixture of pyridine and piperidine. 2-Aminopyridine, in dilute hydrochloric acid solution, in presence of colloidal platinum or platinum black, absorbs hydrogen with quantitative formation of 2-iminopiperidine hydrochloride. The free base can be obtained from the hydrochloride by means of silver oxide, but is hydrolysed, on boiling in aqueous solution, to 2-piperidone. In neutral aqueous solution, 2-aminopyridine hydrochloride is hydrogenated in presence of platinum oxide with formation of piperidine and ammonia. 2-Iminopiperidine hydrochloride could not be reduced in neutral aqueous solution in presence of platinum black, but yielded piperidine and ammonia in presence of platinum oxide. 1-Methyl-2-pyridone yielded 1-methyl-2-piperidone when treated with hydrogen in presence of platinum black in hydrochloric acid solution. The following corrected m. p. are reported: piperidine hydrochloride, 244·5°, piperidine picrate, 150·5°, and 1-benzoyl-2-piperidone, 120°. F. G. W.

Action of Organo-magnesium Compounds on Nitriles. P. Bruylants (*Bull. Acad. Roy. Belg.*, 1924, [v], **10**, 126—140).—The action of magnesium methyl bromide and other organo-magnesium compounds on various *tert.*-α-aminonitriles (cf. A., 1923, i, 762) yields no ketones, but proceeds almost exclusively in accordance with the scheme: $CN{\cdot}CHR{\cdot}N{<}+MgR'X \longrightarrow MgX{\cdot}CN+CHRR'{\cdot}N{<}$; in certain cases, the accessory reaction, $2CN{\cdot}CHR{\cdot}N{<}+2MgR'X \longrightarrow 2MgX{\cdot}CN+R'{\cdot}R'+{>}N{\cdot}CHR{\cdot}CHR{\cdot}N{<}$, also takes place.

The action of magnesium methyl bromide on α-piperidinopropiononitrile (cf. Knoevenagel, A., 1904, i, 990) yields *iso*propylpiperidine (cf. Ladenburg, A., 1882, 535, 1194) and βγ-*dipiperidinobutane*, $(CHMe{\cdot}C_5H_{10}N{\cdot})_2$, which is a colourless liquid, b. p. 294—297°/763 mm., has the normal molecular weight in freezing benzene, and forms a *chloroaurate*, m. p. 210—215° (decomp.), and a *chloroplatinate*, m. p. 255° (decomp.).

With piperidinoacetonitrile, magnesium methyl bromide yields (1) ethylpiperidine (cf. Ladenburg, A., 1882, 534), the picrate of which has m. p. 165° (Dennstedt, A., 1890, 1429, gave m. p. 163°), and (2) a small proportion of a compound, b. p. 200—220°, not yet identified.

α-*Piperidinobutyronitrile*, $C_5H_{10}N{\cdot}CHEt{\cdot}CN$, prepared by the interaction of propionaldehyde, piperidine hydrochloride, and potassium cyanide, is a colourless liquid with a faint odour, b. p. 218—220° (slight decomp.), 108—110°/17 mm., d_4^{20} 0·9245, n_D^{20} 1·4628. With magnesium methyl bromide it yields: (1) *methylethylpiperidinomethane*, $C_5H_{10}N{\cdot}CHMeEt$, which is a colourless liquid with a pronounced basic odour, b. p. 175—176°/768·4 mm., d_4^{20} 0·8378, n_D^{20} 1·4506, and forms a microcrystalline *picrate*, m. p. 96—98°, and a *methiodide* crystallising in long needles, m. p. 210—212° (decomp.); (2) a small amount of a product of higher boiling point. With magnesium phenyl bromide, it forms *phenylethylpiperidinomethane*, $C_5H_{10}N{\cdot}CHPhEt$, which is a colourless liquid, b. p. 275—276°/769·5 mm., d_4^{20} 0·9549, n_D^{20} 1·5251, exhibits the normal molecular weight in freezing benzene, and forms an uncrystallisable methiodide. With magnesium benzyl bromide it gives *benzylethylpiperidinomethane*, $C_5H_{10}N{\cdot}CHEt{\cdot}CH_2Ph$, which is a colourless liquid, b. p. 293—295°/770 mm., d_4^{20} 0·9431, n_D^{20} 1·5198, and shows normal cryoscopic behaviour in benzene.

α-Diethylaminovaleronitrile, prepared from diethylamine hydrochloride, potassium cyanide, and butyronitrile, is a colourless liquid, b. p. 94—96°/17 mm., d_4^{20} 0·8545, n_D^{20} 1·4315, with an odour recalling those of the amine and aldehyde. With magnesium ethyl bromide it yields *ethylpropyldiethylaminomethane*, $NEt_2\cdot CHEtPr$, which is a colourless liquid, b. p. 174°/772 mm., d_4^{20} 0·7736, n_D^{20} 1·4243, and has the normal molecular weight in freezing benzene.

T. H. P.

Piperidine Derivatives. A Cyclic and an Open-chain Compound Related in Structure to Cocaine. S. M. McElvain (*J. Amer. Chem. Soc.*, 1924, **46**, 1721—1727).—Ethyl 4-benzoxy-1-methylpiperidine-3-carboxylate hydrochloride has been prepared. It is as toxic as cocaine, but is a less effective anæsthetic. The corresponding open-chain compound, β-carbethoxyethyl-γ-benzoxypropylmethylamine, $CH_2OBz[CH_2]_2\cdot NMe[CH_2]_2\cdot CO_2Et$, prepared for comparison, is only about one-third as toxic as the piperidine derivative, but scarcely produces anæsthesia. Methylamine hydrochloride and ethyl β-bromopropionate in alcoholic solution condense in the presence of silver oxide, giving *ββ′-dicarbethoxydiethylmethylamine*, $NMe(CH_2\cdot CH_2\cdot CO_2Et)_2$, b. p. 136—138°/4 mm., d_{20}^{20} 1·0190, n_D^{20} 1·4411 (yield 65%), which is converted by sodium and xylene into *ethyl* 1-*methyl*-4-*piperidone*-3-*carboxylate*, b. p. 114—116°/4 mm., d_{20}^{20} 1·0660, n_D^{20} 1·4802 (*hydrochloride*, m. p. 128—129°) (yield 57%). This keto ester tends to isomerise on standing, yielding a product which is probably an internal quaternary salt, whilst reduction with platinum oxide catalyst in alcoholic solution (cf. this vol., i, 417) converts it into *ethyl* 4-*hydroxy*-1-*methylpiperidine*-3-*carboxylate*, a viscous, colourless oil, b. p. 122—124°/4 mm., d_{20}^{20} 1·0879, n_D^{20} 1·4742. The hydrochloride of the latter is converted by benzoyl chloride into *ethyl* 4-*benzoxy*-1-*methylpiperidine*-3-*carboxylate hydrochloride*, m. p. 181—183°. β-Bromopropionic acid and methylamine condense in aqueous solution in the presence of sodium hydrogen carbonate, and the product on esterification gives a 37% yield of ethyl β-methylaminopropionate, b. p. 59—61°/4 mm., d_{20}^{20} 1·0082, n_D^{20} 1·4443 (cf. Gansser, A., 1909, i, 702), and 11% of ββ′-dicarbethoxydiethylmethylamine. Ethyl β-methylaminopropionate and trimethylenechlorohydrin at 140—150° yield *β-carboxyethyl-γ-hydroxypropylmethylamine*, b. p. 123—125°/2 mm., d_{20}^{20} 1·0190, n_D^{20} 1·4450, whilst with γ-chloropropyl benzoate *β-carbethoxyethyl-γ-benzoxypropylmethylamine hydrochloride*, m. p. 103—105°, is obtained.

R. B.

Tertiary Aminoketones and their Use in Ring Syntheses. K. H. Bauer and K. Bühler (*Arch. Pharm.*, 1924, **262**, 128—136).—Compounds of the type $CH_2Ph\cdot NPh\cdot CH_2\cdot CO\cdot R$ should suffer intramolecular condensation to give either *iso*quinoline or indole derivatives (cf. Mannich and Kuphal, A., 1912, i, 850; Rügheimer and Schön, A., 1909, i, 605). Actually the latter reaction takes place exclusively; thus, *benzylphenylaminoacetone*,

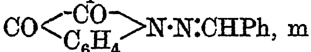
$$CH_2Ph\cdot NPh\cdot CH_2\cdot COMe,$$

b. p. 320—334°, produced by interaction of benzylaniline and chloroacetone in a sealed tube at 100°, the *hydrochloride* of which has m. p. 193°, undergoes this condensation when treated in hot xylene with phosphorus pentoxide, yielding 1-*benzyl*-3-*methylindole*, m. p. 75°, b. p. 340—350° (*picrate*, m. p. 167°). Similarly, ω-bromoacetophenone and benzylaniline give directly in cold alcohol 1-*benzyl*-3-*phenylindole*, needles, m. p. 108°. This yields a *hydrochloride*, m. p. 160°, and when distilled over zinc dust breaks down into toluene and 2-phenylindole. (As 3-phenylindole is converted into the 2-isomeride when heated with zinc chloride, the formation of 2-phenylindole here is considered not to be surprising.) Even when a *m*-hydroxy group is present in the benzyl radical—an introduction that should facilitate the *iso*quinoline condensation—the reaction takes the same course; thus, m-*hydroxybenzylaniline*, prisms, m. p. 103—104°, obtained by reducing *m*-hydroxybenzylideneaniline, affords, when treated with ω-bromoacetophenone, 1-m-*hydroxybenzyl*-3-*phenylindole*, rhombohedra, m. p. 148—149°, the *picrate* of which forms prisms, m. p. 112°. When the compound is distilled over zinc dust, it yields *m*-cresol and 2-phenylindole. *Methyl* 5-*chloromethylsalicylate* prepared by treating methyl salicylate with chloromethyl ether and hydrochloric acid, forms needles, m. p. 68°, and when acted on by sodium methoxide is converted into *methyl* 5-*methoxymethylsalicylate*, needles, m. p. 118°, whilst with diazomethane it affords *methyl* 2-*methoxy*-5-*chloromethylbenzoate*, an oil, b. p. 165—170°/22 mm., and with ammonia, or *via* the *phthalimido* compound (prisms, m. p. 160—162°) it yields *methyl* 5-*aminomethylsalicylate*, an oil, the *hydrochloride* of which has m. p. 122°; with aniline, *methyl* 5-*phenylaminomethylsalicylate*, $NHPh\cdot CH_2\cdot C_6H_3(OH)\cdot CO_2Me$, scales or needles, m. p. 107°, is obtained, and when this is treated in a sealed tube at 120° with chloroacetone, a semi-solid substance is produced which is converted into 1-(4-*hydroxy*-3-*carbomethoxybenzyl*)-3-*methylindole*, prisms, m. p. 99—100°, when treated in hot xylene solution with phosphorus pentoxide. W. A. S.

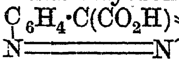
Isatin and Related Compounds. V. Nitroisatins. W. Borsche, H. Weussmann, and A. Fritzsche (*Ber.*, 1924, **57**, [*B*], 1149—1152).—A preliminary note induced by the recent communications of Rupe and Stöcklin (this vol., i, 764) and of Karrer and Haebler (this vol., i, 722).

5-Nitroisatin is converted by hydroxylamine hydrochloride and sodium hydroxide into 5-*nitroisatic acid oxime*, m. p. 209—210°, and 5-*nitroisatoxime*, decomp. 225°. 5-*Nitroisatinhydrazone* forms yellow needles, decomp. above 300°. 5-Nitroisatin is converted by malonic acid in hot glacial acetic acid solution into 6-*nitro*-2-*hydroxyquinoline*-4-*carboxylic acid*, m. p. above 300°. 1-Methylisatin is converted by sulphuric acid and potassium nitrate into 5-*nitro*-1-*methylisatin*, m. p. 203° [*hydrazone*, m. p. 210° (decomp.)]. Isatoxime is converted at 230° into *o*-aminobenzonitrile, but an analogous reaction with 5-nitroisatoxime could not be effected. 6-*Nitroisatoxime*, m. p. 238—239°, is prepared by the action of nitrous acid on 6-nitro-oxindole.

p-*Nitroisonitrosoacetanilide*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH{:}N{\cdot}OH$, m. p. 204—206°, is prepared from *p*-nitroaniline, hydroxylamine, and chloral hydrate in boiling aqueous solution; the corresponding meta and ortho *compounds*, m. p. 181° and 142°, respectively, are also described. The conversion of these compounds into isatins has not yet been effected satisfactorily. The *diisonitrosoacetyl* derivative of p-*phenylenediamine*, which is unchanged below 285°, is converted by concentrated sulphuric acid at 70—80° into 5-*isonitrosoacetylaminoisatin*, a reddish-brown powder which does not change below 285°; in this instance, condensation occurs at only one side of the molecule. H. W.

N-Aminoisatin. R. STOLLÉ and W. BECKER (*Ber.*, 1924, 57, [*B*], 1123—1124; cf. Neber and Keppler, this vol., i, 761).—Benzylidenephenylhydrazine and oxalyl chloride in ethereal solution yield the *compound*, $CHPh{:}N{\cdot}NPh{\cdot}CO{\cdot}COCl$, m. p. 110° (corresponding *anilide*, m. p. 200°), which passes at 150° or when treated with aluminium chloride in the presence of carbon disulphide into 1-*benzylideneaminoisatin*,  $\mathrm{CO}{<}\begin{smallmatrix}\mathrm{\cdot CO\cdot}\\ \mathrm{C_6H_4}\end{smallmatrix}{>}\mathrm{N{\cdot}N{:}CHPh}$, m. p. 147°. The latter compound is oxidised by hydrogen peroxide in alkaline solution to *o*-benzylidenehydrazinobenzoic acid,

$$CHPh{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H,$$

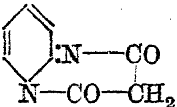
m. p. 224°. 1-Benzylideneaminoisatin is transformed by boiling hydrochloric acid into benzaldehyde and indazole-3-carboxylic acid, m. p. 258° (decomp.) (acetyl derivative, m. p. 188°), and by sodium hydroxide solution into 3-*phenylcinnoline*-4-*carboxylic acid*,  $\begin{array}{l}\mathrm{C_6H_4{\cdot}C(CO_2H)} \\ | \\ \mathrm{N{=\!=\!=\!=}N}\end{array}{>}\mathrm{CPh}$, m. p. 244° (decomp.). H. W.

The Characteristic of Pyridone Tautomerism. A. E. TSCHITSCHIBABIN and N. P. JELETZKY (*Ber.*, 1924, 57, [*B*], 1158—1161).—It has not previously been found possible to decide whether the conversion of 2-alkoxypyridines into 1-alkylpyridones occurs directly or through the intermediate production of quaternary alkyl halides. Since, however, 2-phenoxypyridine is convertible by heat into 1-phenylpyridone, it is established that direct conversion is possible.

1-*Phenyl*-2-*quinolone*, m. p. 138°, is prepared by heating the potassium derivative of carbostyril with bromobenzene and copper powder at 250°. 2-Phenoxypyridine is converted at a red heat partly into 1-phenyl-2-pyridone; under similar conditions, 2-phenoxyquinoline gives 1-phenyl-2-quinolone. The potassium derivative of carbostyril and allyl bromide give 1-*allyl*-2-*quinolone*, b. p. 326—329°, the *chloroplatinate* of which is described. An attempt to prepare 2-allyloxyquinoline by the action of 2-chloroquinoline on a solution of sodium in allyl alcohol yielded 1-allyl-2-quinolone. H. W.

Tautomerism of 2-Aminopyridine. II. Formation of Dicyclic Derivatives of 2-Aminopyridine. A. E. TSCHITSCHIBABIN (*Ber.*, 1924, 57, [*B*], 1168—1172).—The ability of

2-aminopyridine to react in the tautomeric pyridone-2-imine form is shown by its power to condense with ethyl malonate and allied compounds to form pyrimidine derivatives. Thus, 2-aminopyridine and ethyl malonate at 165—195° yield 4 : 6-*diketo*-1 : 2-*divinylene*-1 : 4 : 5 : 6-*tetrahydropyrimidine* (annexed formula), decomp. 295—298° when rapidly heated, which is converted by concentrated nitric acid into 5-*nitro*-4 : 6-*diketo*-1 : 2-*divinylenetetrahydropyrimidine*, decomp. 255°. With ethyl methylmalonate 2-aminopyridine yields 4 : 6-*diketo*-5-*methyl*-1 : 2-*divinylenetetrahydropyrimidene*, decomp. 302—303°, and with ethyl ethylmalonate it gives 4 : 6 - *diketo* - 5 - *ethyl* - 1 : 2 - *divinylenetetrahydropyrimidine*, decomp. 260°; it does not appear to react analogously with ethyl diethylmalonate. The action of even a large excess of ethyl oxalate on 2-aminopyridine gives only *di-2-pyridyloxamide*, $(CO{\cdot}NH{\cdot}C_5H_4N)_2$, m. p. 161—162°, which is also formed when the substances react in absolute alcoholic solution in the presence of sodium alkoxide; under the latter conditions, ethyl malonate does not yield the pyrimidine derivative described above. H. W.



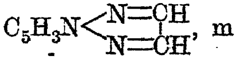
Preparation of Hydroxycarboxylic Acids from Hydroxypyridines. A. E. Tschitschibabin and A. W. Kirssanow (*Ber.*, 1924, **57**, [*B*], 1161—1163).—The sodium salt of 2-pyridone or freshly-distilled 2-pyridone in the presence of ignited, powdered potassium hydroxide is converted by carbon dioxide under 20 atmospheres pressure at 180—200° into 2-hydroxypyridine-5-carboxylic acid, m. p. 304° (decomp.). The synthesis is analogous to Kolbe's synthesis of salicylic acid, from which it differs in that the carboxyl group enters in the para and not the ortho position to the hydroxyl group. When, as in carbostyril, the para position is occupied the synthesis does not appear to take place even under conditions more drastic than those outlined above. H. W.

Diazotisation and Nitration of 4-Aminopyridine. E. Koenigs, G. Kinne, and W. Weiss (*Ber.*, 1924, **57**, [*B*], 1172—1178).—4-Chloropyridine-2 : 6-dicarboxylic acid is converted by concentrated aqueous ammonia into *ammonium hydrogen 4-aminopyridine-2 : 6-dicarboxylate*, m. p. 299° (corr.), from which 4-*aminopyridine-2 : 6-dicarboxylic acid*, m. p. 297° (corr.), is readily isolated. The *copper hydrogen* salt, the *carbethoxy* derivative, m. p. 304° (corr.) after previous softening, the *benzoyl* derivative, m. p. 309° (corr.), and the *ethyl* ester, m. p. 149—151° [*hydrochloride*, m. p. 283—284°, and *chloroaurate*, m. p. 178° (corr.) of the latter], are described. The acid is converted by distillation with lime into 4-aminopyridine [*chloroaurate*, m. p. 283—284° (corr.); *chloroplatinate*, m. p. 251—252° (corr.); *picrate*, m. p. 215—216° (corr.); *hydrogen sulphate*; *benzoyl* derivative, m. p. 202° (corr.)]. 4-Aminopyridine can be diazotised by cautious addition of nitrosylsulphuric acid to its solution in fuming nitric acid; the product is converted in the usual manner into 4-*pyridylazoresorcinol*,

$$C_5H_4N{\cdot}N{:}N{\cdot}C_6H_3(OH)_2,$$

4-*pyridylazodimethylaniline dinitrate*, m. p. 76—77° (corr.), and

4-*pyridylazo*-m-*phenylenediamine*, m. p. 263—264° (corr.). 4-*Nitroaminopyridine*, $C_5H_4N{\cdot}NH{\cdot}NO_2$, m. p. 243—244° (corr.), is most conveniently prepared by the cautious addition of nitric acid (*d* 1·52) to a solution of 4-aminopyridine in concentrated sulphuric acid; the *hydrochloride*, m. p. 240° after softening at 210°, *nitrate*, m. p. 202—204° (corr.), *chloroplatinate*, m. p. 209° (corr.), *sodium* salt, m. p. 260—261°, *potassium* salt, m. p. 301—302°, and *benzoyl* derivative, m. p. 226° (corr.), are described. 4-Nitroaminopyridine is reduced by stannous chloride and concentrated hydrochloric acid to 3 : 4-diaminopyridine which could not be isolated in the homogeneous condition (during the action a partial isomerisation of 4-nitroamino- into 3-nitro-4-amino-pyridine appears to take place); the *chloroplatinate*, m. p. 231—232° (corr.), and the *dibenzoyl* derivative, m. p. 213° (corr.), are described. The diamine condenses with glyoxal to form 3 : 4-*pyridopyrazine*,

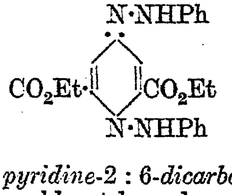


$C_5H_3N{<}\begin{matrix}N{=}CH\\ \quad\;|\\ N{=}CH\end{matrix}$, m. p. 153° [*chloroplatinate*, m. p. 248—249° (corr.)]. H. W.

Products of the Nitration of 4-Aminopyridine. E. Koenigs, M. Mields, and H. Gurlt (*Ber.*, 1924, 57, [*B*], 1179—1187; cf. Koenigs, Kinne, and Weiss, preceding abstract).—An extended examination of the primary product of the nitration of 4-aminopyridine has shown it to be 4-nitroaminopyridine instead of the expected 3-nitro-4-aminopyridine. The substance is converted by diazotisation in concentrated hydrochloric acid solution or by evaporation with concentrated hydrochloric acid into 4-chloropyridine; under the latter conditions a *dichloropyridine*, needles which sublime at 160°, is also produced [*additive* compound with mercuric chloride, m. p. 246—248° (decomp.)]. The nitroamine is reduced by zinc dust and sodium hydroxide solution to 4-hydrazinopyridine, which could not be isolated in the homogeneous condition, but is characterised by several derivatives (Koenigs and Zscharn, unpublished work). 4-Nitroaminopyridine is transformed by concentrated sulphuric acid at 160° into 3-*nitro*-4-*aminopyridine*, m. p. 200° (*hydrochloride*, m. p. 258—259°; *chloroplatinate*, m. p. 256°; *picrate*, m. p. 197—198°). Treatment of 4-aminopyridine dissolved in concentrated sulphuric acid with nitric acid (*d* 1·52) results in the production of 3-*nitro*-4-*nitroaminopyridine*, m. p. 202° (decomp.); the very unstable *hydrochloride*, the *picrate*, m. p. 188—189°, and the *potassium* salt are described. The compound can also be prepared by the nitration of 4-nitroaminopyridine, but not from 3-nitro-4-aminopyridine. If 4-aminopyridine is nitrated as described above and the solution is heated for a short time at 170—175°, 3 : 5-*dinitro*-4-*aminopyridine*, m. p. 170—171°, is produced; the *picrate*, m. p. 147° (indef.), the *chloroaurate*, m. p. 228—229°, and the *disodium* salt are described. 3-Nitro-4-aminopyridine is converted by boiling barium hydroxide solution into 3-*nitro*-4-*hydroxypyridine*, m. p. 284° (decomp.), identical with the product described by Koenigs and Freter (following abstract). Reduction of 3-nitro-4-aminopyridine with stannous chloride and concentrated hydrochloric acid yields 6-*chloro*-3 : 4-*diaminopyridine*, m. p. 162° [*hydro-*

chloride ($+\frac{1}{2}H_2O$), m. p. 218°; *chloroplatinate*; *dibenzoyl* derivative, m. p. 218°]; the substance can be diazotised in dilute hydrochloric acid solution, thus establishing beyond doubt the presence of an amino group in position 3. Similarly, 3 : 5-dinitro-4-aminopyridine is converted by stannous chloride and concentrated hydrochloric acid into 2 : 6-*dichloro*-3 : 4 : 5-*triaminopyridine*, m. p. 206°; the *hydrochloride*, $C_5H_6N_4Cl_2,HCl,H_2O$, m. p. 220°, is described. 3-Nitro-4-aminopyridine is converted by bromine in glacial acetic acid solution into a mixture of 3-*nitro*-4-*aminopyridine hydrobromide* ($+3H_2O$), m. p. 266°, and 5-*bromo*-3-*nitro*-4-*aminopyridine*, m. p. 181° (*chloroplatinate*, m. p. 276°).

Ethyl acetonedioxalate is converted by phenylhydrazine in boiling alcoholic solution into *ethyl* 1-*anilino*-4-*phenylhydrazonodihydropyridine*-2 : 6-*dicarboxylate* (annexed formula), m. p. 194°, which could not be reduced to aminopyridinedicarboxylic acid. H. W.



Nitration of 4-Hydroxypyridine. E. Koenigs and K. Freter (*Ber.*, 1924, **57**, [*B*], 1187—1192).—3-Nitro-4-hydroxypyridine, m. p. 269—270° (decomp.), is prepared by adding 4-*hydroxypyridine nitrate*, m. p. 190°, to a cold mixture of nitric acid (*d* 1·52) and fuming sulphuric acid (70% SO_3) and subsequently heating the mixture to gentle ebullition; the product appears to be identical with the substance, m. p. 284° (decomp.), described by Koenigs, Mields, and Gurlt (preceding abstract). 5-*Bromo*-3-*nitro*-4-*hydroxypyridine*, prepared from 3-nitro-4-hydroxypyridine and bromine water, has m. p. 370° after darkening at 350°. Protracted heating of 4-hydroxypyridine with a mixture of fuming nitric and sulphuric acids leads to the formation of 3 : 5-*dinitro*-4-*hydroxypyridine*, m. p. 325°; the *monohydrate* and the *monosodium* salt, m. p. 314—315°, are described. Phosphorus pentachloride converts 3-nitro-4-hydroxypyridine into 4-chloro-3-nitropyridine, which, probably by reason of the extreme lability of the halogen atom, could not be obtained in the homogeneous state; the *chloroplatinate*, m. p. 222° (decomp.), and the *picrate*, m. p. 120°, are described. The substance is converted by hot water into 3-nitro-4-hydroxypyridine and by aqueous ammonia into 3-nitro-4-aminopyridine. Under certain conditions, it is transformed by an alcoholic solution of sodium ethoxide into 3-*nitro*-4-*ethoxypyridine*, m. p. 49—50° [*hydrochloride*, m. p. 160°; *chloroplatinate*, m. p. 246—248° (decomp.)]. Reduction of 3-nitro-4-ethoxypyridine by stannous chloride and concentrated hydrochloric acid gives 6-*chloro*-3-*amino*-4-*ethoxypyridine*, m. p. 73° (*chloroplatinate*, decomp. above 280°; *picrate*, m. p. 197°). 3-*Nitro*-4-*hydrazinopyridine* has m. p. 200°. H. W.

Antiseptic Action of Anil-pyridines and Anil-quinolines. C. H. Browning, J. B. Cohen, S. Ellingsworth, and R. Gulbransen (*J. Path. Bact.*, 1924, **27**, 121—122; cf. *Brit. Med. J.*, 1923, II, 326).—In general, the anil series shows a marked resemblance to the analogous styryl series in possessing marked antiseptic properties. In both series, alterations in the side-chain occupying the 6-position are not very marked in their effect.

CHEMICAL ABSTRACTS.

Derivatives of Quinoline. S. LOEWE (D.R.-P. 380918; from *Chem. Zentr.*, 1924, i, 1446).—The following compounds are mentioned: 2-β-*Aminoethylquinoline*; its *dipicrate*, m. p. 202°; 2-β-*methylaminoethylquinoline*; its *picrate*, m. p. 185—188°; 2-β-*piperidylethylquinoline*; its *dipicrate*, leaflets, m. p. 145° (decomp.); 4-β-*dimethylaminoethylquinoline*; its *dipicrate*, yellow, crystalline powder, m. p. 203°.

G. W. R.

Manufacture of Alkyloxyacridines. L. CASSELLA & Co., G.M.B.H. (Brit. Pat. 217715).—Hydroxyacridines may be converted into *O*-alkyl ethers, without the nitrogen being alkylated, by the action of alkylating agents in the presence of acid-binding substances; *e.g.*, a mixture of mono- and di-methoxyacridines is obtained by stirring 3 : 6-dihydroxyacridine, dissolved in aqueous sodium hydroxide, with methyl sulphate. The preparation of the following is described: 3 : 6-*Dimethoxyacridine*, pale yellow crystals, m. p. 138—139°, giving a green fluorescence in acid solution; 3 : 6-*dihydroxyacridine monomethyl ether*, small, bright yellow crystals, m. p. above 300°, giving a green fluorescence in acid solution; 3 : 6-*diethoxyacridine*, yellow needles, m. p. about 142—143°; 3 : 6-*dihydroxyacridine monoethyl ether*, yellow crystals, m. p. above 300°, giving a green fluorescence in concentrated sulphuric acid; 3 : 6-*dimethoxy*-2 : 7-*dimethylacridine* (from the hydroxy-base and methyl *p*-toluenesulphonate), straw-coloured needles, m. p. 235—238°, giving a green fluorescence in sulphuric acid; 3 : 6-*dihydroxy*-2 : 7-*dimethylacridine monomethyl ether*, a bright yellow solid, m. p. above 300°; 3 : 6-*dihydroxyacridine di*-β-*hydroxyethyl ether* (from 3 : 6-dihydroxyacridine and ethylene chlorohydrin), reddish-yellow crystals, m. p. 200°, giving a slight green fluorescence in concentrated sulphuric acid. The new compounds are non-toxic and are valuable bactericides.

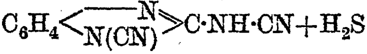
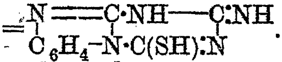
W. T. K. B.

Pyrimidines. VI. New Colour Tests for Uracil and Cytosine. O. BAUDISCH (*J. Biol. Chem.*, 1924, **60**, 155—166).—If uracil or cytosine be treated with ferrous hydrogen carbonate and air, a brilliant lemon-yellow pigment is formed by subsequent autoxidation. Dihydro*iso*barbituric acid is first produced. After filtration from the ferric hydroxide and further exposure to air, this is converted into the deep red ferrous salt of *iso*barbituric acid and, by further autoxidation, the solution changes colour from the surface downwards to bright yellow. The yellow colour develops much more quickly from cytosine than from uracil, the ammonia produced from the former acting as a catalyst and hastening autoxidation. The yellow compound has not been obtained in sufficient quantity for analysis, but its chemical reactions are described. In alkaline solutions, it has an oxidation-reduction power which is well shown with methylene-blue; it reduces ammoniacal silver nitrate and phosphomolybdic acid, giving a deep blue colour with the latter. Diazobenzenesulphonic acid gives an intense, but temporary, brilliant red colour. These tests are very delicate. The chemical properties of uracil and cytosine are compared with those of indole and anthracene compounds and other substances widely distributed in plants and animals, and their significance in biochemical processes is discussed. It is considered that the pyrimidines or their decomposition products possess the functions of respiration pigments. C. T. G.

Alkylation of Indazoles. K. VON AUWERS and H. G. ALLARDT (*Ber.*, 1924, 57, [*B*], 1098—1106).—In continuation of previous investigations (Auwers and Schaich, A., 1921, i, 806), the effect of experimental conditions on the formation of 1- or 2-alkylindazoles has been systematically examined. The action of ethyl iodide on the alkali derivatives of indazole leads preferentially to the production of 2-ethylindazole, whereas 1-ethylindazole predominates when the mercury or silver salt is employed. Since, however, indazole sodium is converted by methyl iodide or benzyl chloride at 100° almost exclusively into 2-methyl- or 1-benzyl-indazole, respectively, the results have no bearing on the constitution of salts of indazole. The preferential formation of 1-alkylindazoles at higher temperatures (cf. *loc. cit.*) does not appear to be a general phenomenon; the effect of concentration is not manifested in one particular direction. Comparative alkylations with methyl, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, allyl, and benzyl bromides indicate that the production of 1-alkyl derivatives is predominating in the cases of the allyl, benzyl, and *iso*propyl compounds, in which the halogen atom is particularly reactive, but, in these cases, the course of the change is not entirely independent of the particular halogen atom present in the halide.

The following new alkylindazoles are described incidentally. 2-iso*Propylindazole*, b. p. 140—142°/15 mm., and the corresponding *picrate*, m. p. 138—140°; 1-*methyl*-2-iso*propylindazolium iodide*, m. p. 132—135° (corresponding *picrate*, m. p. 191—192·5°), which passes when heated into 1-methylindazole and *iso*propyl iodide; 2-*methyl*-1-iso*propylindazolium iodide*, m. p. 183°, which yields 1-*iso*propylindazole when heated; 1-n-*butylindazole*, b. p. 135—136°/13 mm. (*picrate*, m. p. 92°), and 2-n-*butylindazole*, b. p. 153°/13 mm. (*picrate*, m. p. 140·5°); 1-iso*butylindazole*, b. p. 133°/16 mm. (*picrate*, m. p. 72·5—73·5°), and 2-iso*butylindazole*, b. p. 150—152°/13 mm. (*picrate*, m. p. 122—123°); 2-p-*nitrobenzylindazole*, m. p. 91—91·5° (the *picrate* exists in two forms, dark yellow crystals and long, flesh-coloured needles, m. p. 142—143°); the constitution of the substance is established by its conversion successively into 2-p-*aminobenzylindazole*, m. p. 117—118°, and the known 2-benzylindazole; 2-o-*nitrobenzylindazole*, m. p. 72·5—73·5° (the *picrate*, m. p. 147°, appears to exist in three modifications). H. W.

Action of Cyanogen Halides on Phenylhydrazine. IX. o-Phenylenethioammeline. G. PELLIZZARI (*Gazzetta*, 1924, 54, 451—456; cf. A., 1921, i, 620; 1922, i, 585; this vol., i, 771).—When treated with ammonium hydrosulphide, αβ-dicyano-*o*-

phenyleneguanidine unites with a molecule of hydrogen sulphide to form *o*-phenylenethioammeline,  $C_6H_4{<}^{\overline{\quad N}}_{N(CN)}{>}C{\cdot}NH{\cdot}CN + H_2S$  $= \begin{matrix} N & = & C{\cdot}NH & - & C{:}NH \\ | & & | & & | \\ C_6H_4 & - & N{\cdot}C(SH){:}N & & \end{matrix}$. The fact that this compound remains unchanged on protracted boiling with concentrated hydrochloric acid indicates that the carbimido group occupies the β- and not the α-position, since in the latter case such group would be converted into carbonyl by this treatment. When its alkaline solution is boiled, *o*-phenylenethioammeline loses hydrogen sulphide and is converted into the *o*-phenyleneammeline obtained by the action of hydrochloric acid on phenylenemelamine (*loc. cit.*), together with phenylenediguanide and phenyleneguanylcarbamide, which are products of the decomposition of *o*-phenyleneammeline.

Thus, in the union of a molecule of a primary amine with αβ-dicyano-*o*-phenyleneguanidine, the melamine nucleus is closed by means of the nitrogen atom of the amine in such a manner that the alkyl group remains connected directly with the nucleus to form an *iso*melamine derivative. When, however, a molecule of hydrogen chloride or sulphide combines with αβ-dicyano-*o*-phenyleneguanidine, the closure of the nucleus is necessarily effected by the nitrogen of one of the two cyanogen groups, the other nitrogen atom forming the carbimido group; the chlorine atom is fixed in the position corresponding with the β-cyanogen, but the sulphydryl group enters in the α-position. Although the chloro derivative reacts readily with amines, the thio compound does not react in this way.

o-*Phenylenethioammeline* forms hard, white, crystalline aggregates (decomp. above 300°), and has a slightly acid character.

T. H. P.

Quinazolines. XXXVI. A Quinazoline Analogue of Cinchophen (Atophan). Synthesis of New Quinazolinecarboxylic Acids from Isatin and from *o*-Aminoacetophenone. M. T. BOGERT and F. P. NABENHAUER (*J. Amer. Chem. Soc.*, 1924, **46**, 1702—1707).—When treated with benzoyl chloride and potassium hydroxide, isatin affords benzoylisatoic acid (yield, 38%), $NHBz{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$, m. p. 167—168°. This, when heated at 150° with alcoholic ammonia (cf. Bischler, A., 1891, 745), is converted into 2-*phenylquinazoline*-4-*carboxylic acid*, pale yellow needles, m. p. 150—151°, a quinazoline analogue of cinchophen (2-phenylquinoline-4-carboxylic acid), which it resembles in certain properties. Both compounds lose carbon dioxide when heated, thus yielding the corresponding 2-phenyl-quinazoline or -quinoline. Acetylisatoic acid, m. p. 152—154° (cf. Suida, A., 1878, 586), is obtained (yield, 86%) by oxidising *o*-acetoaminoacetophenone with potassium permanganate below 0° (cf. Glücksmann, A., 1890, 1416) and is converted by alcoholic ammonia at 100—110° into 2-*methylquinazoline*-4-*carboxylic acid*, pale yellow, thick prisms (dihydrate), m. p. 175·5—176·5°, giving 2-methylquinazoline when heated. Other acyl derivatives of isatoic acid may be obtained similarly.

Thus o-*phthaloylaminoacetophenone*, prisms, m. p. 151·5°, from *o*-aminoacetophenone and phthalic anhydride in benzene solution, yields *phthaloylisatinic acid*, $CO_2H·C_6H_4·CO·NH·C_6H_4·CO·CO_2H$, scales, m. p. 151·5°, which with methyl-alcoholic ammonia at 140° yields 2-o-*carboxyphenylquinazoline-4-carboxylic acid*, platelets, m. p. 188—189°. Preliminary physiological tests have been made on the *diammonium* salt of this acid. Acyl derivatives of *o*-aminoacetophenone themselves condense with alcoholic ammonia, yielding quinazolines. Thus *o*-phthaloylaminoacetophenone yields 2-o-*carboxyphenyl-4-methylquinazoline*, needles, m. p. 185—186° (decomp.). o-*Methoxalylaminoacetophenone*,

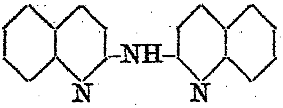
$$CO_2Me·CO·NH·C_6H_4·Ac,$$

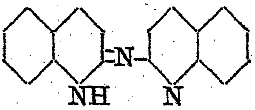
needles, m. p. 128°, from methyl oxalate and *o*-aminoacetophenone, and o-*oxamaminoacetophenone*, $NH_2·CO·CO·NH·C_6H_4·Ac$, m. p. 238°; both yield 4-*methylquinazoline-2-carboxylic amide*, pale yellow prisms, m. p. 235·5°, which is converted into 4-methylquinazoline by boiling hydrochloric acid. *o*-Aminoacetophenone is converted by methyl iodide and methyl alcohol at 100° into o-*dimethylaminoacetophenone*, a pale yellow oil, b. p. 91—94°/1·5 mm. (*picrate*, m. p. 183—184°).

R. B.

Synthesis of an Azocyanine. (Miss) F. M. HAMER (*J. Chem. Soc.*, 1924, **125**, 1348—1357).—Azocyanines are analogues of the cyanine dyes having a nitrogen atom as a link between the quinoline nuclei. By heating 2-aminoquinoline with 2-chloroquinoline the hydrochloride of 2 : 2′-diquinolylamine is obtained (4-aminoquinoline does not so react). This substance exists in two modifications (I) and (II), according to the theory of Scheibe (cf. A., 1921, i, 451). The action of methyl iodide on this substance produces a mixture of 2 : 2′-diquinolylamine hydriodide ($C_{18}H_{14}N_3I$) and the azocyanine, 1-methyldihydroquinolenyl-2-quinolyl-2′-imine methiodide (III). A second method of preparation is that of converting the acetyl derivative of 2 : 2′-diquinolylamine first into its dimethosulphate, which with sodium hydroxide gives 1-methyldihydroquinolenyl-2-quinolyl-2′-imine, then treating the base with hydriodic acid. A comparison with the analogous 1 : 1′-dimethylpseudo*iso*cyanine iodide shows that the replacement of ⁚CH· by ⁚N· causes a shift of the absorption bands towards the more refrangible region of the spectrum.

(I.)





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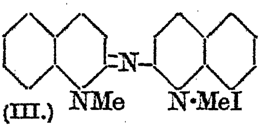


(III.)

A. COUSEN.

Derivatives of 2-Aminopyridine, 2-Aminoquinoline, and 4-Aminoquinoline. E. DIEPOLDER [with K. DACHLAUER, E. DEUERLEIN, and E. WOLFEL] (*J. pr. Chem.*, 1923, **106**, 41—65).—The chief product of the interaction of 2-chloropyridine and o-aminophenol is 2-*o*-hydroxyphenylimino-1 : 2-dihydropyridine

(Steinhauser and Diepolder, A., 1916, i, 739). Its *hydrochloride* (white plates, m. p. 153—154°), *picrate* (yellow needles, m. p. 170—173°), *chloroplatinate* [dark yellow plates, m. p. 180° (decomp.)], *mercurichloride*, $C_{11}H_{10}ON_2,HCl,2HgCl_2$ (colourless needles, m. p. 149—151°), and *mercuric chloride additive* compound,

$$C_{11}H_{10}ON_2,2HgCl_2$$

(fine needles, m. p. 160—162°), are now described. With nitrous acid, it yields the 1-*nitroso* derivative, yellowish-brown needles, m. p. 275—276° (decomp.).

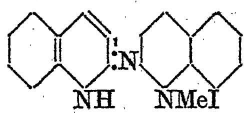
The *methiodide*, pale brown prisms, m. p. 188—191° (decomp.), when dissolved in sodium hydroxide solution, loses hydrogen iodide and gives 2-o-*hydroxyphenylimino*-1-*methyl*-1 : 2-*dihydropyridine* (needles, m. p. 116—117°), isomeric with the product (m. p. 159°), previously obtained from 2-chloropyridine and *o*-anisidine.

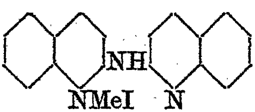
o-*Hydroxyphenyl*-2 : 2′-*dipyridylamine*, $OH\cdot C_6H_4\cdot N(C_5H_4N)_2$, is produced by heating 2-chloropyridine (2 mols.) and *o*-aminophenol (1 mol.) in sealed tubes in presence of zinc chloride or barium oxide. It forms white needles, m. p. 187°, and is formed as a by-product in the preparation of the above imine. The *hydrochloride*, a white, flocculent precipitate, has m. p. 242—244° (sintering at 132°). The *chloroplatinate*, orange-yellow needles, m. p. 212—215°; *chloroaurate*, orange plates, m. p. 195°; *picrate*, yellow needles, m. p. 190°; *mercurichloride*, needles, m. p. 206—208°; *mercuric chloride additive* compound, white prisms, m. p. 169—172°, are described.

2 : 2′-Dipyridylamine, from 2-amino- and 2-chloro-pyridine, forms a *mercurichloride*, $C_{10}H_9N_3,HCl,HgCl_2$ (colourless needles, m. p. 225° with previous sintering), and a *methiodide* (yellow prisms, m. p. 288—291°), stable to cold alkali and losing methyl iodide, not hydrogen iodide, when warmed with alkali.

2 : 2′-*Diquinolylamine*, from 2-amino- and 2-chloro-quinoline, white needles, m. p. 161°, does not react with benzaldehyde. The following derivatives are described: *Hydrochloride*, yellow prisms, m. p. above 305°; *chloroaurate*, orange needles, m. p. 306°; *mercurichloride*, pale yellow prisms, m. p. 272°; *monopicrate*, yellow plates, m. p. 286°; *dipicrate*, yellow needles, m. p. 297° (decomp.); *nitrosoamine*, pale yellow needles, m. p. 238° (decomp.). It forms a *monomethiodide*, yellow plates, m. p. 246—278° (decomp.), stable to cold alkali. Presumably this has formula (I), as hydriodic acid (not, as is the case, methyl iodide) should be removed by the action of alkali if (II) were the formula.

(I.)





(II.)

4 : 4′-*Dimethyl*-2 : 2′-*diquinolylamine*, yellow prisms, m. p. 167·5°, was formed by the interaction of 2-chloro-4-methylquinoline and 2-amino-4-methylquinoline. The *hydrochloride*, yellow prisms, m. p. 292—297°; the *mercurichloride*, needles, m. p. 249°; *chloroplatinate*, yellow needles, m. p. 280° (decomp.); the *mono*-

picrate, yellow needles, decomp. at 286—299°; the *dipicrate*, dark yellow needles, decomp. at 265—289°; *nitrosoamine*, pale yellow needles, decomp. 238°, and the *methiodide*, yellow prisms, sintering at 245°, m. p. (decomp.) 290°, are described. The methiodide loses methyl iodide when warmed with alkali.

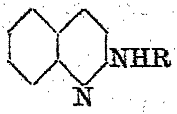
2-*Pyridyl-2′-quinolylamine*, obtained similarly, forms pale yellow plates sintering at 104°, m. p. 108°. The *hydrochloride*, yellow needles, m. p. 215—216° (decomp.); *monopicrate*, needles, m. p. 242—244°; *mercuric chloride additive* compound, pale yellow needles, m. p. 210°; *mercurichloride*, pale yellow prisms, m. p. 245°; *methiodide*, yellow plates, m. p. 208° (giving methyl iodide with warm alkali), are described.

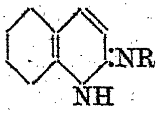
2-*Pyridyl-4′-methyl-2′-quinolylamine*, from 2-aminopyridine and 2-chloro-4-methylquinoline, forms pale yellow prisms, sintering at 158°, m. p. 174°. The *hydrochloride*, needles, m. p. 241°, and the *methiodide*, yellow prisms, m. p. 208°, decomposed by warm alkali, are described.

4-*Methyl-2 : 2′-diquinolylamine* forms yellow prisms, m. p. 129° (darkening at 126°). The *hydrochloride*, pale yellow needles, m. p. 267—275° (decomp.); *monopicrate*, yellow prisms, m. p. 287° (decomp.), and the *methiodide*, long, yellow prisms, m. p. 247—253° (decomp.), decomposed by warming with alkali, are described.

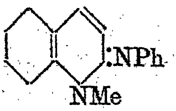
These bases are peculiar in that they only give monomethiodides, these being readily decomposed on warming with alkalis.

Note on the Substituted Aminoquinolines.—The experimental part of this work is not yet described, but a summary is given. Two possible formulæ (III) or (IV) exist for the substituted 2-(or 4-)-aminoquinolines:

(III.)




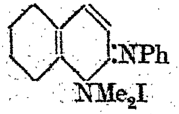
(IV.)

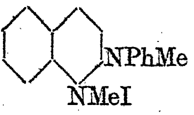


(V.)

Hitherto in no cases have the isomerides been found to exist side by side, but two methyl derivatives have now been isolated. The substituted aminoquinolines are formed by the interaction of the chloroquinoline and the corresponding amine, and the methyl derivatives (*e.g.*, V) are formed by the action of alkali on the methiodide.

The methiodide (VI) differs from that (VII) formed by the interaction of 1-methyl-2-iodoquinolinium iodide and methylaniline.

(VI.)




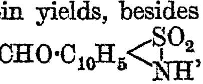
(VII.)

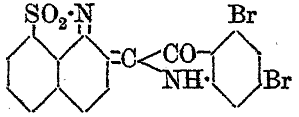
The 4-phenylamino derivative also gives a methiodide differing from that prepared by the interaction of methylaniline and 1-methyl-4-iodoquinolinium iodide.

With nitrous acid, these amines give 1-*nitroso* derivatives. The position of the nitroso radical is shown by the fact that they are not basic and are not converted by alcoholic hydrogen chloride into *p*-nitroso derivatives.

Neither 2-aminoquinoline nor its methiodide reacts with aldehydes, although 2-aminopyridine readily does so. A. E. C.

Some Derivatives of 1 : 8-Naphthasultam. W. König and E. Wagner (*Ber.*, 1924, **57**, [*B*], 1056—1061; cf. Zincke, A., 1916, i, 426; 1917, i, 38; 1918, i, 550).—The analogy between 1 : 8-naphthasultam and α-naphthol can be further traced in their indole-indigotin derivatives, and the relative positions of the absorption bands of 2-naphthalene-2′-indole-indigotin and 2-naphthasultam-2′-indole-indigotin (1 : 8-sultam-2-naphthalene-2′-indole-indigo) are similar, the different values obtained in the latter case from those given by Friedländer and Sander (this vol., i, 662, 663) being attributed to the use of different solvents. Analogies are also observed between *N*-phenyl- and *N*-*p*-tolyl-1 : 8-naphthasultam and the α-naphthol derivatives (α-naphthyl phenyl ethers), which couple rapidly with diazotised 2 : 4-dinitroaniline in acetic acid solution (cf. K. H. Meyer, A., 1914, i, 882) yielding dyes the absorption curves of which suggest that the coupling has taken place in the *p*-position. The partial removal of the aryl residue observed in the case of α-naphthyl phenyl ether was not detected.

2-*Naphthasultam*-2′-[5′ : 7′-*dibromoindole*]-*indigotin* (annexed formula), dark blue needles, subliming about 200°, obtained by converting 5 : 7-dibromoisatin into its chloride with phosphorus pentachloride in benzene solution, and heating this with naphthasultam, resembles dibromo-2-naphthalene-2′-naphtholindigotin. On heating with 10% sodium hydroxide solution, 2-naphthasultam-2′-indole-indigotin yields, besides anthranilic acid, 1 : 8-*naphthasultam-2-aldehyde*,  $CHO{\cdot}C_{10}H_5{<}^{SO_2}_{NH}$, small, colourless crystals, decomp. above 200°, giving a yellow *sodium* salt. N-*Phenylnaphthasultam*, colourless needles, m. p. 158°, from phosphoryl chloride and potassium *N*-phenyl-1-naphthylamine-8-sulphonate, couples with 2 : 4-dinitrobenzenediazonium sulphate, yielding 4-[2′ : 4′-*dinitrobenzeneazo*]-N-*phenyl*-1 : 8-*naphthasultam*, reddish-brown needles, m. p. 240°, giving a yellowish-red solution in alcohol gradually changed through red, violet, and blue to green by alkali. On nitration in the usual way, *N*-phenylnaphthasultam yields 4-nitro-1-phenylaminonaphthalene-8-sulphonic acid, whilst nitration in acetic acid gives 4-*nitro*-N-*phenyl*-1 : 8-*naphthasultam*, long, yellow needles, m. p. 200°, yielding 4-*amino*-N-*phenyl*-1 : 8-*naphthasultam*, deep yellow lancets, m. p. 185°, which after diazotisation couples with β-naphthol and R-salt, giving bright red dyes. N-p-*Tolylnaphthasultam*, m. p. 152°, similarly obtained from sodium *N*-*p*-tolyl-1-naphthylamine-8-sulphonate, gives 4-[2′ : 4′-*dinitrobenzeneazo*-]-N-p-*tolyl*-1 : 8-*naphthasultam*, m. p. 195°. *N*-Methyl-1 : 8-naphthasultam couples with diazotised 2 : 4 : 6-trinitroaniline in acetic acid solution, yielding 4-[2′ : 4′ : 6′-*tri*-



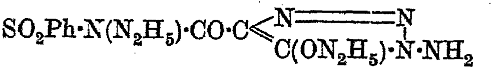
nitrobenzeneazo]-N-*methyl*-1 : 8-*naphthasultam*, red needles, m. p. 293°, whilst *N*-methyl-*p*-toluenesulphonyl-α-naphthylamine does not couple. R. B.

The Interaction of Benzenesulphonazide and Ethyl Malonate. T. Curtius and G. Ehrhart (*J. pr. Chem.*, 1923, [ii], **106**, 66—75).—When a mixture of benzenesulphonazide and ethyl malonate is boiled at 110°/20—25 mm. for some hours, then shaken with alkali and neutralised in the cold with acid, the first product is 5-*hydroxy*-1-*benzenesulphonyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*, a yellow oil, which slowly isomerises to the corresponding triazolone, a solid, forming weakly anisotropic rhombohedra, decomp. 106°.

The *ethyl* ester is best prepared by treating the sulphonazide with ethyl sodiomalonate in alcohol, adding water, cooling, and acidifying. A viscous oil is produced which behaves as an *enol* towards ferric chloride; on keeping, it isomerises to the solid triazolone, anisotropic rhombs, which melt at 79° and slowly evolve nitrogen at 110°.

The products of acid hydrolysis of the triazolone ester are benzenesulphonamide, glycollic acid, nitrogen, and carbon dioxide, indicating that the keto-group is in position (5). Its stability to concentrated hydrochloric acid and the fact that nitrogen is only eliminated very slowly on heating, and not at all by the addition of iodine, indicate that it is not a diazo derivative of the formula $SO_2Ph{\cdot}NH{\cdot}CO{\cdot}C(:N_2)CO_2Et$. However, the ester reacts with ammonia and hydrazine as if it possessed a diazo structure. With aqueous ammonia under pressure, the *ammonium* salt of 5-*hydroxy*-1-*benzenesulphonyl*-1 : 2 : 3-*triazole*-4-*carboxylamide* is produced which on acidification yields the free hydroxy compound as a viscous oil; this isomerises into 5-*hydroxy*-1 : 2 : 3-*triazole*-4-*benzenesulphonylcarboxylamide*, $SO_2Ph{\cdot}NH{\cdot}CO{\cdot}C_2HON_3$, anisotropic prisms which decompose on heating.

By the action of hydrazine on the ester, nitrogen and ammonia were evolved, and the *hydrazine* salt of 1-*amino*-5-*hydroxy*-1 : 2 : 3-*triazole*-4-*benzenesulphonylcarboxylamide* (annexed formula) was produced as small plates, which on neutralisation gave the free hydroxyamide as small, colourless prisms.

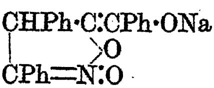


$$SO_2Ph{\cdot}N(N_2H_5){\cdot}CO{\cdot}C{<}\begin{matrix}N{=\!=\!=\!=}N\\ C(ON_2H_5){\cdot}N{\cdot}NH_2\end{matrix}$$

This substance affords a *benzylidene* derivative, forming colourless anisotropic prisms. A. E. C.

***iso*Oxazoline Oxides. II. Benzoyldiphenylisoxazoline Oxide.** E. P. Kohler (*J. Amer. Chem. Soc.*, 1924, **46**, 1733—1747; cf. this vol., i, 571).—Phenylated derivatives of the *iso*oxazoline oxide previously obtained (*loc. cit.*) have now been prepared. These do not form additive compounds with water etc., and are not ruptured by strong bases, whilst acid chlorides and anhydrides only act as dehydrating agents. Phenylnitromethane and styryl methyl ketone condense in methyl-alcoholic sodium methoxide solution, giving γ-*nitro*-βγ-*diphenylpropiophenone*,

NO_2·CHPh·CHPh·CH_2Bz, in two stereoisomeric forms, m. p. 181—182° and 131—132°, the former predominating, especially in boiling solutions. Bromination of the isomeride, m. p. 181—182°, in chloroform solution yields two stereoisomeric α-*bromo* derivatives, m. p. 185° and 162°, the isomeride of m. p. 131—132° similarly yielding two other isomeric α-*bromo* derivatives, m. p. 155° and 125—127°. Bromination of the nitroketone in the presence of sodium methoxide yields γ-*bromo*-γ-*nitro*-βγ-*diphenylpropiophenone* in two stereoisomeric forms, m. p. 178—180° (decomp.) and 136—138°, differing from the α-bromo compounds in their readier decomposition by heat and their stability towards potassium acetate. All four α-bromo compounds lose hydrogen bromide when treated with methyl-alcoholic potassium acetate, yielding in the case of the isomerides from the nitroketone of m. p. 181—182° a single oxide, 4-*benzoyl*-2 : 3-*diphenyl*iso*oxazoline oxide*, m. p. 123° (+1MeOH, m. p. 93°), and, with the bromo derivatives of the lower-melting isomeride, a mixture of this oxide and an *isomeric* iso*oxazoline oxide*, flat needles, m. p. 151°.



$$\begin{array}{l}\text{CHPh·C:CPh·ONa}\\ \;|\qquad\;\;>\text{O}\\ \text{CPh=N:O}\end{array}$$

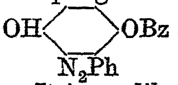
The former oxide yields a colourless *sodium* derivative (annexed formula), converted by benzoyl chloride into the *benzoate*, $C_{29}H_{21}O_4N$, needles, m. p. 190°. The sodium derivative gradually becomes yellow in dilute solution, but gives no copper derivative. When oxidised by sodium peroxide, the lower-melting oxide gives benzoic acid and the colourless sodium salt of the *enolic* form (m. p. 113°) of 2 : 3-*diphenylisoxazol*-4-*one* (*copper* derivative, deep blue). A boiling ethereal solution of the enol deposits the *ketonic* form in hard, lustrous tablets, m. p. about 150° (decomp.), the structure of which is established by its synthesis by the action of hydroxylamine hydrochloride on a methyl-alcoholic solution of *methyl benzoylphenylacetate*, CHBzPh·CO_2Me, m. p. 75°, obtained by the alcoholysis of benzoylphenylacetonitrile. Solutions of the oxides in concentrated alkalis are colourless, but on dilution beyond a certain point turn yellow, through formation, together with *iso*oxazole, of αγδ-*triphenylbutanetrione oxime*, HON:CPh·CHPh·COBz, by opening of the *iso*oxazole ring.

The oxime, which is most conveniently obtained by the action of alcoholic alkali on the bromine compound, crystallises with 1 mol. of ether. The ether-free substance has m. p. 150°, decomposing immediately afterwards. It gives no copper derivative; strong bases convert it almost quantitatively into *iso*oxazole, and oxidation with sodium peroxide yields benzoic acid and benzil β-monoxime, m. p. 118°. (Benzil β-monoxime, m. p. 113—114°, dissolved in sodium hydroxide and reprecipitated with hydrochloric acid, melts sharply at 118°.) The *iso*oxazoline oxides on treatment with organic or inorganic bases or with acetyl chloride or phosphorus pentachloride readily lose water, giving the *iso*oxazole. 4-*Benzoyl*-2 : 3-*diphenyl*iso*oxazole*, lustrous prisms, m. p. 167°, is most easily obtained by the action of ammonia on the lower-melting oxide in methyl-alcoholic solution. The structure of the *iso*oxazole is deduced (1) from its reduction by zinc and acetic acid to 2 : 3-*diphenyl*-4-(*hydroxybenzyl*)iso*oxazole*, which is oxidised back to the ketone by chromic acid, and yields the corresponding *tertiary alcohol*, m. p. 145°, with magnesium ethyl bromide; and (2) from the behaviour of its *oxime*, m. p. 177°, which with phosphorus pentachloride in dry ether undergoes a Beckmann transformation, yielding the *imide chloride*, $C_{15}H_{10}ON(CPh{:}NCl)$, yellow prisms, m. p. 139°, and an *anilide*, $C_{22}H_{16}O_2N_2$, colourless prisms, hydrolysed by alcoholic potassium hydroxide to 2 : 3-*diphenyl*-iso*oxazole*-4-*carboxylic acid*, thin plates, m. p. 170°. This acid gives an ozonide converted by water into oxalic acid and β-benzilmonoxime, m. p. 118°. On treatment with magnesium ethyl bromide etc., the *iso*oxazoline oxide affords a *tertiary alcohol*, bunched needles, m. p. 168°, which with alcoholic potassium hydroxide gives the above tertiary alcohol (m. p. 145°). The same product is obtained when the reaction mixture is allowed to reach room temperature, boiled, and decomposed with acid, excess of Grignard reagent merely acting as a dehydrating agent and the system ·CPh:NO remaining unattacked, behaviour which shows that the *iso*oxazoline oxides do not contain a nitro group. R. B.

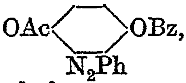
Synthesis Reactions of Benzthiazole and its Derivatives. G. Bruni and T. G. Levi (*Gazzetta*, 1924, **54**, 402—410; cf. A., 1921, i, 734; 1922, i, 466, 755).—Each of the following compounds yields (1) 1-anilinobenzthiazole when heated with sulphur and aniline at temperatures below 200°, and (2) 1-thiolbenzthiazole when heated with sulphur under pressure at above 260°: monophenylthiocarbamide, thiocarbanilide, *s*-phenyldimethylthiocarbamide, phenylguanidine, *s*-diphenylguanidine, monophenyldiguanide, phenylcyanamide. Benzthiazole itself is formed in such syntheses less frequently than its derivatives but is obtained in small proportion when methyleneaniline is heated with sulphur and aniline at temperatures below 200°; with sulphur under pressure above 300°, methyleneaniline reacts to form 1-thiolbenzthiazole.

T. H. P.

Oxidation of Benzeneazoquinol. D. Bigiavi and B. de Benedetti (*Gazzetta*, 1924, **54**, 363—376).—To some extent benzeneazoquinol and the isomeric azoxy derivatives derived therefrom are subject to the influence of the 1 : 4-positions of the two hydroxyl groups. Thus, oxidation of benzeneazoquinol to the azoxy compounds by means of peracetic acid takes place only if one or both of the hydroxyls are protected by introduction of benzoyl or acetyl groups. Moreover, the action of bromine on α-benzeneazoxyquinol does not lead to definite compounds, a bromine atom apparently entering the quinol nucleus and brominating the monobenzoyl derivative of the azoxy compound. This benzoyl derivative is converted into a nitro derivative by the action of nitrous acid, which, however, oxidises α-benzeneazoxyquinol to α-benzeneazoxyquinone. The latter exhibits certain properties of quinonoid compounds. Thus it is yellow, is readily prepared by the action of lead peroxide on the acetic acid solution of the corresponding quinol, is rapidly reduced to α-benzeneazoxyquinol by phenylhydrazine or hydroxylamine, and liberates iodine from potassium iodide solution faintly acidified with acetic acid. On the other hand, it is non-volatile, is not reduced by sulphurous acid, and does not form with azoxyquinol compounds of the quinhydrone type.

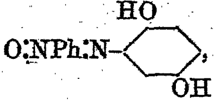
Benzeneazobenzoylquinol, prepared by coupling diazobenzene with monobenzoylquinol, has the structure  $\underset{N_2Ph}{OH\langle\quad\rangle OBz}$ and may be regarded as an *o*-hydroxyazo compound. It is readily oxidised by peracetic acid, with formation of the two isomeric azoxy derivatives. Of these, the one which must be regarded as the α-isomeride reacts with bromine to form first a monobromo derivative and ultimately a mixture of products difficult to separate and yielding aniline as sole volatile base on reduction. Unlike this α-compound, the isomeric β-benzeneazoxybenzoylquinol does not react with nitrous acid.

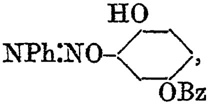
Benzeneazoquinol, prepared by hydrolysis of benzeneazobenzoylquinol (cf. Witt and Johnson, A., 1893, i, 571), forms black crystals with cantharides-green reflection, or a garnet-red powder, m. p. 149°. With nitrous acid, it yields, not a nitro derivative but a *compound*, $C_{12}H_8O_2N_2$, which forms bright red crystals, blackening at 160°, m. p. 172°, and may be benzeneazoquinone or a polymeride thereof.

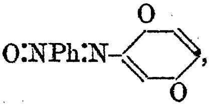
Benzeneazobenzoylacetylquinol,  $\underset{N_2Ph}{OAc\langle\quad\rangle OBz}$, obtained by acetylating benzeneazobenzoylquinol, forms orange-yellow needles, m. p. 111°.

Benzeneazodibenzoylquinol, $C_{28}H_{18}O_4N_2$, separates in orange-yellow, crystalline globules, m. p. 153—155°, and *benzeneazodiacetylquinol* in orange, crystalline granules, m. p. 112°.

α-Benzeneazoxybenzoylquinol, $O:NPh:N\cdot C_6H_3(OH)\cdot OBz$, forms a pale yellow, crystalline powder, m. p. 167°, and dissolves slowly in alkali solution giving a violet-red liquid. *α-Benzeneazoxybenzoylacetylquinol*, $O:NPh:N\cdot C_6H_3(OAc)\cdot OBz$, forms golden-yellow scales, transparent, red, rhombic crystals $(+2C_2H_4O_2)$, or white or pale yellow crystals, m. p. 133°. *α-Benzeneazoxydibenzoylquinol* forms white crystals, m. p. 146—146·5°, and *α-benzeneazoxydiacetylquinol* an almost white, crystalline powder, m. p. 111—113°.

α-Benzeneazoxyquinol,  $O:NPh:N-\overset{HO}{\underset{OH}{\langle\quad\rangle}}$, forms golden-yellow chips, blackening at about 162°, m. p. 166°, dissolves to a violet-blue solution in alkali hydroxide solution, and darkens on exposure to light. *α-Benzeneazoxybenzoylbromoquinol* [OH : Br : OBz=2 : 3 : 5], separates as a pale yellow, crystalline powder, m. p. 197°; *α-benzeneazoxybromoquinol* forms yellowish-brown, silky needles, m. p. 188—191° (decomp.), and *α-benzeneazoxybenzoylnitroquinol*, yellow globules, m. p. 149—150°. *α-Benzeneazoxynitroquinol* forms rosettes of chestnut-yellow needles, darkening at 175°, m. p. 188° (slight decomp.), and dissolves to a blue liquid in alkali hydroxide or carbonate solution.

β-*Benzeneazoxybenzoylquinol*,  crystallises in yellow needles, m. p. 120—121°. β-*Benzeneazoxyquinol* forms garnet-red crystals, m. p. 151°, and gives blood-red, ruby-red, and brownish-red solutions in alkali hydroxide solution, ammonia solution, and concentrated sulphuric acid respectively; in acetic acid solution, it reacts with lead peroxide, the product being apparently β-benzeneazoxyquinone, since by similar means α-benzeneazoxyquinol is oxidised to α-*benzeneazoxyquinone*,



which forms quinone-yellow, plush-like needles, m. p. 133° (decomp.), and colours alkali hydroxide solutions yellowish-brown when cold or violet-blue when heated. T. H. P.

Remarkable Reaction of Phenylhydrazine. Syntheses of Azo Dyes from 2-Methylated Quinolinium and Indolenium Salts. E. ROSENHAUER (*Ber.*, 1924, **57**, [*B*], 1192—1194).—The production of an azo dye from 2-bromomethylquinoline methobromide and phenylhydrazine (this vol., i, 768) is explained by the observation of the simultaneous formation of aniline and ammonia, the unstable hydrazo compound which is intermediately formed being reduced by the excess of phenylhydrazine. The tendency to form azo dyes in this manner is unusually pronounced, since they can also be produced from unsubstituted 2-methylquinolinium and -indolenium salts. Thus 1 : 2 : 3 : 3-tetramethylindolenium iodide and phenylhydrazine at about 120° yield 2-*benzeneazomethylene*-1 : 3 : 3-*trimethylindoline hydriodide*, decomp. 240°, from which the corresponding *base*, m. p. 106—107°, is prepared by the action of ammonia. H. W.

2-Hydrazinocymene and Other Compounds derived from 2-Aminocymene. W. A. DEMONBREUN and R. E. KREMERS (*J. Amer. Pharm. Assoc.*, 1923, **12**, 589—592).—2-*Hydrazinocymene hydrochloride* has m. p. 186—187°; *acetyl* derivative, m. p. 125—126°; *dextrose* compound, m. p. 92—93°; *mannose* compound, m. p. 110°; *galactose* compound, m. p. 149—150°. *Cymylcarbamide* has m. p. 162—163°; s-*cymylphenylcarbamide* has m. p. 192°. CHEMICAL ABSTRACTS.

Derivatives of *p*-Phenylenedihydrazine. (Preliminary Note.) R. STOLLÉ and K. LEFFLER (*Ber.*, 1924, **57**, [*B*], 1061—1063).—Attempts to obtain better yields of the additive compound from azodibenzoyl and dimethylaniline (A., 1912, i, 920) by using a solvent were fruitless; the use of the more stable but more unsaturated azodicarboxylic ester with aromatic hydrocarbons leads in the presence of sulphuric acid to derivatives of *p*-phenylenedihydrazine, $C_6H_4[N(CO_2R)\cdot NH\cdot CO_2R]_2$, the constitution of which follows from their decomposition to *p*-phenylenediamine and phenylhydrazine. Thus methyl azodicarboxylate and benzene yield *methyl* p-*phenylenedihydrazinetetracarboxylate* (m. p. 209°; yield 90%), this with sodium hydroxide yielding phenylhydrazine and *p*-phenylenediamine, with pyridine, *p*-phenylenediamine and a yellow *substance*, m. p. 235°, and with acetic acid *p*-phenylenediamine. *Ethyl* p-*phenylenedihydrazinetetracarboxylate*, m. p. 192°, is similarly obtained from ethyl azodicarboxylate and benzene, whilst toluene gives a resinous product yielding *p*-tolylhydrazine with sodium hydroxide, and bromobenzene gives a 70% yield of *p*-bromophenylhydrazine. R. B.

Rate of Diazotisation of Amines. M. L. WILLARD (*Textile Colorist*, 1924, **46**, 164—165; cf. *ibid.*, 1924, **46**, 22).—The rate of diazotisation of aniline and *p*-toluidine in *N*-solution is compared with that in solutions of 0·001*N* (Hantzsch and Schumann), 0·01*N* (Tassilly, A., 1914, ii, 42, 190, 256), and 0·1*N* concentration. Increased concentration of the amine acclerates the reaction but is less stable. At 20° the reaction with aniline is almost twice as fast as at 0°. The temperature effect on *p*- and *m*-toluidine was not quite so pronounced as with aniline. At higher temperatures, reaction is not quantitative, owing to decomposition, with the formation of tarry matter, and from most of the amines gas was evolved even at 20°. The reaction velocity of nitrous acid with amines containing negative radicals, anthranilic acid, and Schäffer's salt, as compared with those containing positive radicals, *p*- and *m*-toluidine, does not differ greatly, but as a whole indicates a slightly greater velocity for the negative amines. The position of the positive or negative radical with regard to the amine radical does not appreciably affect the reaction velocity.

CHEMICAL ABSTRACTS.

Biological Standardisation of Salvarsan and Neosalvarsan. G. B. ROTH (*U.S. Pub. Health Service, Hyg. Lab. Bull.*, 1924, No. 135, 13—32).—Salvarsan is about twice as toxic as neosalvarsan to the mouse, rat, and guinea pig. CHEMICAL ABSTRACTS.

Aromatic Compounds containing Arsenic and Antimony. I. Phenylenearsinicstibinic Acids. H. SCHMIDT (*Ber.*, 1924, **57**, [*B*], 1142—1148).—Compounds containing the arsinic and stibinic acid residues attached to the same benzene nucleus can be obtained by treating diazotised aminophenylarsinic acids with antimony oxide or from arsenite and diazotised aminophenylstibinic acids. p-*Phenylenearsinicstibinic acid*,

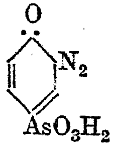
$$[C_6H_4(AsO_2)\cdot SbO_2,H_2O,4H_2O]_x,$$

is a colourless powder prepared by the successive addition of solutions of tartar emetic and sodium hydroxide to a diazotised solution of *p*-aminophenylarsinic acid. It exhibits the phenomenon of gradual neutralisation with alkali hydroxide, the rate depending on the concentration of the hydroxyl ions, the temperature, and the particular cation. The steps in the process of neutralisation are not sufficiently sharply differentiated to allow conclusions to be drawn as to the degree of polymerisation of the compound. The acid is converted by ammonium chloride in hydrochloric acid solution into the *compound* $[AsO_3H_2 \cdot C_6H_4 \cdot Sb(OH)Cl_3]_3[NH_3]_2,6H_2O$, and by pyridine hydrochloride into the *substance*

$$(AsO_3H_2 \cdot C_6H_4 \cdot SbCl_4)_2,(C_5H_5NHCl)_2,1\tfrac{1}{3}H_2O.$$

4-*Hydroxyphenylene*-3-*stibinicarsinic acid* is a pale yellow powder which closely resembles the analogous compound described above.

Diazotisation of 3-amino-4-hydroxyphenylarsinic acid in 5*N*-hydrochloric acid solution causes the separation of the diazo compound (annexed formula), decomp. about 150°.



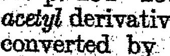
Analysis of the compounds is effected by boiling them with a mixture of concentrated sulphuric acid and nitric acid (*d* 1·49) and subsequent treatment of the solution with ammonium sulphate until the residual nitric acid is destroyed. Arsenic and antimony are then determined in the usual manner. H. W.

Organic Selenium Compounds. III. Preparation of a Selenium Derivative of Cinchophen Type. M. T. Bogert and H. H. Hopkins (*J. Amer. Chem. Soc.*, 1924, **46**, 1700—1701).—6-Amino-2-phenylbenzoselenazole (A., 1922, i, 1182) has been converted by the Sandmeyer reaction into 6-*cyano*-2-*phenylbenzoselenazole*, a brown powder, decomp. 145—150°, which when hydrolysed with sulphuric acid yields 2-*phenylbenzoselenazole*-6-*carboxylic acid*, amorphous, decomp. 170—180° (*methyl* ester, crystals, m. p. 164·5—165·5°). The acid is a selenium derivative of the cinchophen (atophan) type and corresponds with 2-phenylbenzthiazole-6-carboxylic acid (A., 1922, i, 576). R. B.

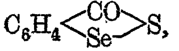
Aromatic Compounds containing Selenium. VI. R. Lesser and R. Weiss (*Ber.*, 1924, **57**, [*B*], 1077—1082; cf. A., 1914, i, 1083).—Selenoxanthone, $C_6H_4{<}{\substack{CO\\Se}}{>}C_6H_4$, m. p. 191—192°, is readily prepared by the action of aluminium chloride on a solution of *o*-chloroselenobenzoyl chloride, $Cl \cdot Se \cdot C_6H_4 \cdot COCl$, in benzene; under similar conditions, toluene yields a *methylselenoxanthone*, m. p. 112—113°. The substance, m. p. 236—237°, obtained by the action of chromic acid on selenoxanthone is an additive compound of chromium trioxide and selenoxanthone oxide,

$$C_{13}H_8O_2Se,CrO_3,$$

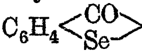
and not of selenoxanthone as considered previously (*loc. cit.*).

o-Chloroselenobenzoyl chloride is converted by ammonia into *benzoyleneselenimide*,  $C_6H_4{<}{\substack{CO\\Se}}{>}NH$, which exists in two forms, needles or plates, m. p. 234—235° after previous softening; the *alkali* salts and the *acetyl* derivative, m. p. 172—174°, are described. The substance is converted by chromic acid into the additive *compound*, C_7H_5ONSe,CrO_3. The corresponding *methylimide*, m. p.

159—160°, *ethylimide*, m. p. 102—103°, *phenylimide*, m. p. 182—183°, and o-*tolylimide*, m. p. 187—188°, are described; *methylenedibenzoyleneselenimide*, $CH_2(C_7H_4ONSe)_2$, has m. p. 331—332°, *o*-Chloroselenebenzoyl chloride is converted by sodium sulphide in the presence of acetone into *benzoyleneselenosulphide*,



$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{Se}>S,$$

m. p. 83—84°. *o*-Chloroselenobenzoyl chloride and hydrogen selenide yield *benzoylenediselenide*,  $C_6H_4<\genfrac{}{}{0pt}{}{CO}{Se}>Se$, m. p. 91—92°.

Dibenzyldiselenide is converted by nitric acid (*d* 1·4) into benzylselenious acid, m. p. 122—123°; the corresponding *barium* ($+2H_2O$) and *calcium* ($6H_2O$) salts are described. The acid is converted by phosphorus pentachloride into dibenzylselenide dichloride, $(CH_2Ph)_2SeCl_2$, m. p. 134—135°. H. W.

Direct Mercurisation of Benzene and the Preparation of Mercury Diphenyl. J. L. Maynard (*J. Amer. Chem. Soc.*, 1924, **46**, 1510—1512; cf. Roeder and Blasi, A., 1915, i, 331).—Phenylmercuric acetate is obtained in 80% yield by boiling benzene (80 c.c.), mercuric acetate (15 g.), and 95% alcohol (20 c.c.) for 55 hours, a further 20 c.c. of alcohol being added after the first 5 hours. A yellow precipitate, due to the alcoholysis of the mercuric acetate at the commencement of the reaction, is redissolved by the addition of a little glacial acetic acid. The acetic acid liberated during the reaction is removed by esterification with the alcohol, the consequent increase in yield of phenylmercuric acetate demonstrating the reversibility of the mercurisation reaction. Mercury diphenyl is obtained in 95% yield by the addition of alkaline sodium stannite solution to a well-stirred suspension of phenylmercuric acetate in cold water (cf. Dimroth, A., 1902, i, 849). F. G. W.

Methylation of the Cerebrosides of Ox Brain. J. Pryde and R. W. Humphreys (*Biochem. J.*, 1924, **18**, 661—664).—Kerasin and phrenosin undergo methylation unchanged. Kerasin takes up five methyl residues to form *pentamethylkerasin*, m. p. 73°. In the case of phrenosin methylation ceased at a stage intermediate between that required for a pentamethyl- and a hexamethyl-phrenosin, the product resembling pentamethylkerasin but having a lower melting point (35—40°). The possibility of the formation of a mixture of two compounds is suggested. The pentamethylkerasin was hydrolysed with acid methyl alcohol. Enough material was obtained to show that it is possible to separate in this way the methylated sugar residue. S. S. Z.

Individual Blood Researches. II. W. Küster and H. Oesterlin (*Z. physiol. Chem.*, 1924, **136**, 279—292).—In the blood of one ox used the α-type of prosthetic group appeared to be preformed in the hæmoglobin, part of it remaining unchanged during the preparation of hæmin by the sulphuric acid–methyl alcohol process, the remainder being converted into the pseudo form of the β-type. In the blood of a second ox of similar age etc., the pseudo form of the α-type appeared to be present. It is considered that in the pseudo form the halogen is bound to nitrogen and not to iron, since it is completely removed by 5% sodium carbonate solution.

The degree of methylation of hæmin prepared from one source of blood was the same whether it was prepared from the whole blood or from the corpuscles. It appears to depend, however, on the amount of cholesterol in the blood. For etherification hydrobromic acid is as satisfactory as hydrochloric acid. O. O.

Absorption of Violet Light by Organic Substances. IV. L. Marchlewski and A. Moroz (*Bull. Soc. chim.*, 1924, [iv], **35**, 705—709).—Derivatives of hæmoglobin and chlorophyll show characteristic absorption bands in the violet part of the spectrum. Coefficients of extinction and absorption curves are given for oxyhæmoglobin, hæmin, hæmatoporphyrin, hæmatoporphyrin hydrochloride, mesoporphyrin hydrochloride, phyllocyanin, and phylloerythrin. R. B.

Porphyrins. VII. Dibromohæmatoporphyrin Dimethyl Ether. W. Küster and H. Oesterlin (*Z. physiol. Chem.*, 1924, **136**, 235—242).—Hæmin is successively converted into chlorodimethylhæmin, *bromodimethylhæmin*, *bromodimethylhæmin dibromide*, and *dibromohæmatoporphyrin dimethyl ether*, $C_{36}H_{42}O_6N_4Br_2$. The last is a reddish-brown, amorphous material possessing no m. p. Its solution in hydrochloric acid showed two absorption bands at 540—568 and 590—600, the ethereal solution giving four bands at 483—520, 527—543, 568—589, 622—630. A *compound* with ammonia, a *silver* salt, a *copper* salt, and a *dimethyl* ester were prepared. From a study of the changes outlined in the scheme above it is concluded that one of the pyrrole nuclei in the porphyrin molecule must exist in the pyrroline form. O. O.

Rational Systematic Classification of Proteins. I. Chromoproteins. H. Steudel and E. Peiser (*Z. physiol. Chem.*, 1924, **136**, 75—81).—Hæmoglobin is resolved by the addition of a trace of hydrochloric acid into its component globin and hæmochromogen or hæmatin. The sodium derivative of hæmatin added to an aqueous solution of globin hydrochloride produces a reddish-brown precipitate which gives analytical figures corresponding with hæmoglobin, but which differs from the latter in solubility, a difference which is ascribed to changes in the globin residue. In aqueous suspension, it behaves to dilute acid as does hæmoglobin. The sodium derivative of hæmatin gives no precipitate with crystallised egg-albumin or globulin, with crystallised serum-albumin, or with protamine sulphate. The general conclusion drawn is that the chromoproteins are salt-like combinations of an acidic with a basic component. J. P.

Rational Systematic Classification of Proteins. II. Chondroproteins. T. Takahata (*Z. physiol. Chem.*, 1924, **136**, 82—88).—The potassium salt of chondroitin sulphuric acid added to clupein sulphate in aqueous solution produces a white precipitate of a protein, *chondroclupein*, containing 47·5% of chondroitin sulphuric acid and 52·5% of clupein. Egg-albumin, edestin, and peptone give no precipitate with chondroitin sulphuric acid, but from collagen a gelatinous *substance* is obtained, composed of 82·5% of collagen and 17·5% of chondroitin sulphuric acid. The chondroproteins are therefore regarded as salt-like compounds (cf. preceding abstract). J. P.

Solubility and Digestibility of Proteins. Z. STARY (*Z. physiol. Chem.*, 1924, **136**, 160—172).—When the insoluble keratins are degraded into soluble products by heating with water under pressure or with dilute alkali, they give rise to soluble products called proto- and deutero-keratoses. These, when obtained by using alkali are extensively racemised. They can be easily salted out, but compared with the normal albumoses they are very resistant towards pepsin and trypsin. When keratins are heated with a mixture of glacial acetic acid and chloro- or bromo-acetic acid, they give rise, without any humin formation, to similar products, which are not racemised, are partly soluble in water and in alcohol, and are only very slightly affected by enzymes. If, however, a keratin such as human hair be treated with glacial acetic acid at the ordinary temperature in presence of an oxidising agent such as bromine, there is very little change in its outward appearance. The product after this treatment is readily soluble in very dilute alkali and is easily hydrolysed by trypsin. It therefore seemed that during this treatment certain reactions such as oxidation and substitution occur with certain groupings in the keratin molecule and alter its properties. With a view to ascertain whether by oxidation certain groups which hinder the action of enzymes are removed, the changes in the properties of keratins after treatment with oxidising agents such as hydrogen peroxide in acid solution and hypohalogen acids have been studied. By gentle oxidation, products result which are slightly soluble in alkali and are dissolved by trypsin. On further oxidation, the solubility in alkali decreases and on strong oxidation the –S–S– linking is attacked, with the formation of sulphuric acid, so that solubility and digestibility by enzymes scarcely seem to bear any relation to the –S–S– linking. D. R. N.

Proteins. I. Behaviour on Solution in Phenols. R. O. HERZOG and E. KRAHN (*Z. physiol. Chem.*, 1924, **134**, 290—295).—Gelatin in phenol solution was heated for varying periods and the product was precipitated with ether. It was found that the amino-nitrogen progressively diminished whilst the total nitrogen remained unchanged; this is interpreted as indicating the formation of diketopiperazines. When wool is treated similarly, a part of the original amino-nitrogen appears as ammonia-nitrogen in the product, and as much as two-thirds of the sulphur may be split off as hydrogen sulphide. C. R. H.

Studies on Proteins. II. Determination of the Molecular Weight of Silk Fibroin. R. HERZOG and M. KOBEL (*Z. physiol. Chem.*, 1924, **134**, 296—299).—The molecular weight of the crystalline substance contained in silk fibroin was determined cryoscopically, using resorcinol as solvent. After preliminary exhaustive extraction of the silk fibroin with water or alcohol, values of about 200 were obtained; after extraction with boiling cresol, 314—380, and after solution in acid and subsequent neutralisation, 350—370. None of these methods of purification affected the nitrogen content of the material to a marked degree. C. R. H.

Catalytic Effect exercised by certain Colloids, especially Glycogen, in the Hydrolysis of Proteins. L. Hugounenq and J. Loiseleur (*Compt. rend.*, 1924, **179**, 86—87).—Without itself undergoing change, lecithin accelerates the hydrolysis of proteins by 0·3% hydrochloric acid, but colloidal silica, alumina, ferric oxide, arsenic sulphide, starch paste, etc. are without effect. Similar positive catalytic actions are exerted by colloidal sodium α-thymonucleate, silver, gold, bismuth, and rhodium, and by glycogen on the hydrolysis by 0·3% sodium hydroxide solution of egg-albumin, fibrin, casein, and nucleoproteins derived from beer-yeast. The extent to which action increases becomes greater as the electric charge of the colloidal substance becomes more marked, and amounts to 30—33% with the colloidal metals. Pure glycogen is devoid of any effect, but becomes active on addition of 0·1% of its weight of an electrolyte such as sodium, potassium, rubidium, calcium, or magnesium chloride; the influence of glycogen increases also with the concentration of the alkali solution used to effect the hydrolysis. T. H. P.

Biochemistry.

Gas and Electrolyte Equilibria in Blood. VI. Acid Properties of Reduced and Oxygenated Hæmoglobin. A. B. Hastings, D. D. Van Slyke, J. M. Neill, M. Heidelberger, and C. R. Harington (*J. Biol. Chem.*, 1924, **60**, 89—153).—The authors have determined directly the base-binding power and buffer value of oxyhæmoglobin and reduced hæmoglobin over the p_H range 6·8 to 7·6. The hæmoglobin was prepared by Heidelberger's method (A., 1922, i, 962) and the experimental technique was that described in the preceding papers of this series (A., 1922, i, 1207; 1923, i, 162, 163). The isoelectric point (I_R) of reduced horse hæmoglobin was found to be at p_H 6·81±0·02. The molecular buffer value (β_R, cf. A., 1922, i, 893) of reduced hæmoglobin is nearly constant between the isoelectric point and p_H 7·6 for a given solution, but increases from 2·6 for 30 m*M* cation concentration to 2·9 for 145 m*M* cation concentration. The buffer value of oxyhæmoglobin decreases steadily from p_H 6·8 to 7·6 and the isoelectric point is estimated to be slightly below p_H 6·7. The increase, $\Delta[BHb]/\Delta[O_2Hb]$, in base-binding power caused by oxygenation of hæmoglobin has a maximum value of about 0·7 equivalent of base per mol. of hæmoglobin; the maximum value occurs at p_H 7·6 in solutions of 30 m*M* cation concentration and at p_H 7·3 in solutions of 145 m*M* cation concentration. This increase in base-binding power at varying p_H on oxygenation of reduced hæmoglobin is shown to follow quantitatively a curve consistent with Henderson's hypothesis (A., 1920, i, 403) that combination with a molecule of oxygen increases the dissociation constant of one acid hydrogen in the hæmoglobin molecule. The results do not follow the equation required by Hill's hypothesis (A., 1922, i, 193, 696; 1923, i, 398, 1144) that only one acid hydrogen in an aggregate of *n* hæmoglobin molecules, where *n* is the index in Hill's oxygen dissociation equation, has its dissociation constant affected by oxygenation and reduction. The relationships between base-binding power, reaction, and degree of oxygenation are expressed by the equation $[BHb] = \beta_R[Hb](p_H - I_R) + [HbO_2](1/1+10^{pK'_o-p_H} - 1/1+10^{pK'_R-p_H})$, where [Hb] indicates total hæmoglobin in mols. of oxygen capacity and $[HbO_2]$ the oxyhæmoglobin. This equation is more accurate than an earlier linear equation (A., 1923, i, 162). Values for the constants of this equation are given for three cation concentrations. E. M. C.

Thermodynamic Relations of the Oxygen- and Base-combining Properties of Blood. W. C. STADIE and K. A. MARTIN (*J. Biol. Chem.*, 1924, **60**, 191—235).—The authors discuss the effect of temperature on the oxygen dissociation curve and base-combining properties of whole blood, and formulate a thermodynamical explanation of these changes. For the equations derived, reference should be made to the original paper. The heats of ionisation of carbonic acid and the hæmoglobin acids are calculated by means of the van't Hoff isochore. The molecular buffer value of hæmoglobin is shown theoretically and by experiment to be independent of temperature. Expressions are derived for the excess of base bound by oxyhæmoglobin over reduced hæmoglobin, and for the effect of temperature on the isoelectric point of a protein. The heats of ionisation of hæmoglobin both as base and acid are shown to be of the same order. It is concluded that, in contrast to its effect on the acid properties, oxidation has probably no effect on the basic properties of hæmoglobin. The magnitude of the heat of ionisation of hæmoglobin as an acid indicates that a small change in temperature produces a large change in the strength of hæmoglobin as an acid. This temperature effect is discussed in relation to fever and a temperature correction factor for p_H is derived.

E. M. C.

Applications of the Donnan Equilibrium to Human Blood-serum. D. W. ATCHLEY, R. F. LOEB, and E. M. BENEDICT (*Proc. Soc. Exp. Biol. Med.*, 1923, **20**, 238).—Dialysis of pure serum solutions and electrolyte solutions *in vitro* reproduced the conditions existing in the body, which are in the nature of the Donnan equilibrium. The serum solution contained less chlorine and more sodium than the fluid outside the collodion sac when potassium was absent; in the presence of potassium, the serum solution contained more potassium, less chlorine, and an equal amount of sodium. The quantitative differences were proportional to the protein concentration in the serum. CHEMICAL ABSTRACTS.

Solution of Fibrin and the Inhibition of Blood Clotting by Nicotine. E. MANGOLD and N. KITAMURA (*Biochem. Z.*, 1924, **147**, 1—6).—In an ultramicroscopic preparation of rabbit or guinea-pig plasma showing formation of fibrin network, the addition of nicotine and its salts produces fibrinolysis. Direct addition of nicotine to the preparation before centrifuging retards or entirely inhibits the clotting and alters the typical form of the fibrin network. J. P.

Increase of Uric Acid in the Blood during Prolonged Starvation. W. G. LENNOX (*J. Amer. Med. Assoc.*, 1924, **82**, 602—604).—During starvation, the uric acid increased from 4 mg. to 10·7 mg. per 100 c.c. of whole blood. In some cases there was decreased excretion of uric acid, but without coincident retention of non-protein or urea nitrogen. CHEMICAL ABSTRACTS.

Calcium in the Blood. W. C. THRO and M. EHN (*Proc. Soc. Exp. Biol. Med.*, 1923, **20**, 313—315).—A low content of calcium in the blood, observed in furunculosis and in pneumonia in young children, is not always observed in tetany. CHEMICAL ABSTRACTS.

Absence of Pyruvic Acid in Blood, Liver, and Muscle. L. J. SIMON and E. AUBEL (*Bull. Soc. Chim. biol.*, 1924, **6**, 424—430).—When pyruvic acid is mixed with an extract of liver or fresh muscle no decrease is observed. When, however, it is injected into the liver *in vivo*, it disappears slowly, and after 1 hour it is possible to recover unaltered only about 40% of the original amount. Alanine, dextrose, and lactic acid under the same conditions do not give rise to pyruvic acid. D. R. N.

Hippuric Acid Metabolism in Man. J. SNAPPER (*Klin. Woch.*, 1924, **3**, 55—56; from *Chem. Zentr.*, 1924, i, 1225—1226).—After administration of 5 g. of sodium benzoate to healthy or diseased men with normal kidneys, 5 g. of hippuric acid are excreted in the urine within 12 hours. Normal kidneys can excrete urine containing up to 2% of hippuric acid. G. W. R.

Transformations of Chlorophyll in the Animal Organism. L. MARCHLEWSKI (*Bull. Soc. Chim. biol.*, 1924, **6**, 464—472).—The pigment termed cholehæmatin by MacMunn and bilipurpurin by Löbisch is shown to be identical with the author's phylloerythrin. It appears in the bile of herbivorous animals only when they are fed on fresh green grass. Cholehæmatin would therefore seem to be derived from chlorophyll, and not from hæmoglobin. D. R. N.

Urine in Pernicious Anæmia. H. REINWEIN and F. THIELMANN (*Arch. Exp. Path. Pharm.*, 1924, **103**, 115—126).—Histidine, methylguanidine, γ-butyrobetaine, *r*-lactic acid, and a base, $C_7H_8O_2N_4$ (probably a dimethylxanthine) have been isolated from [illegible] in cases of pernicious anæmia and identified by analysis. J. P.

Globulin and Albumin Content of the Plasma in Nephritis. G. C. LINDER, C. LUNDSGAARD, and D. D. VAN SLYKE (*Proc. Soc. Exp. Biol. Med.*, 1923, **20**, 320).—In most cases of glomerular nephritis examined, low protein concentrations of 3·5—5·5% were observed; in all cases the albumin : globulin ratios were less than 1 : 4. Cases of nephrosis gave similar results.

CHEMICAL ABSTRACTS.

Relationship between the Calcium and Inorganic Phosphorus of the Serum in Rickets and Tetany. J. HOWLAND and B. KRAMER (*Monatsh. Kinderheilk.*, 1923, **25**, 279—293; from *Chem. Zentr.*, 1924, i, 1221; cf. Kramer, Tisdall, and Howland, A., 1923, i, 412).—In rickets, the phosphorus content of serum is decreased whilst the calcium content remains practically normal. In tetany, the phosphorus content remains normal and the calcium content is decreased. The occurrence of rickets is connected with the product of the calcium and potassium contents, expressed in mg. per 100 c.c. Rickets occurs when this is below 30 and may be excluded when it is above 40. In tetany, the product is generally 30 or slightly less. G. W. R.

Action of Alkali Iodides on Metabolism. E. HESSE (*Arch. Exp. Path. Pharm.*, 1924, **102**, 63—92).—Alkali iodide administered in considerable amount to dogs produces an increase in protein metabolism (nitrogen excretion) and in the gaseous exchange, the latter being conditioned chiefly by the former. In general, alkali iodides are regarded as increasing all chemical and enzymatic reactions in the organism, leading to breakdown of proteins, and possibly also to deamination of the hydrolysis products, more especially in the liver. The effect on protein metabolism of various iodinated fatty acid derivatives is compared with the action of potassium iodide. The action is similar, but may be more marked. Iodival (monoiodo*iso*valerylcarbamide) and alival (iododihydroxypropane) are toxic to dogs. J. P.

Mode of Action of Phosphorus. K. ENGEL (*Arch. Exp. Path. Pharm.*, 1924, **102**, 289—304).—Tonophosphan (an organic compound of phosphorous acid) stimulates the weakly beating mammalian or frog heart, and the surviving mammalian intestine, bladder, and uterus. From comparative experiments it is concluded that the action of tonophosphan is similar to that of sodium phosphite, but in higher concentrations the latter is more toxic than the former. Aqueous solutions of phosphorus act in a similar way to phosphite, but are still more toxic. Sodium hypophosphite is very much less toxic and has no stimulating action. The action of phosphate differs from that of phosphite. J. P.

Irreciprocal Permeability. IV. Salt Effect on the Living Membrane. E. WERTHEIMER (*Pflüger's Archiv*, 1923, **201**, 488—502; from *Chem. Zentr.*, 1924, i, 1207; cf. this vol., i, 686).—Basic dyes dissolved in distilled water or in isotonic solutions of non-electrolytes scarcely diffuse at all through the thoroughly washed membrane of frog's skin, although in electrolytic solu-

tions they diffuse readily. This electrolyte effect is not shown by acid dyes. The permeability of the membrane for sodium chloride is subject to the same salt effect. Sugar, amino-acids, and peptone can only diffuse when the inner side of the membrane is in contact with a non-electrolytic solution. The same effects are not observed with the outer side of the frog's skin, nor with dead membrane.
G. W. R.

Permeability in Non-electrolytic Solutions. K. HIRUMA (*Pflüger's Archiv*, 1923, **200**, 497—510; from *Chem. Zentr.*, 1924, i, 1220).—The absorption by red blood corpuscles of salicylate and thiocyanate is increased, and that of ammonium and alkaloids decreased by sucrose. With frog-muscle, sucrose causes increased absorption of basic dyes, alkaloid salts, iodine, acids, methylamine, salicylate, and thiocyanate. Amino-acids are not absorbed by blood-corpuscles.
G. W. R.

Water–Salt Content of the Body in Relation to the Acid–Base Economy. I. Colloidal Chemical Basis of Purine Diuresis. C. OEHME (*Arch. Exp. Path. Pharm.*, 1924, **102**, 40—62).—Oral administration of caffeine produces in adults a diuresis and an increased excretion of chlorides. Intravenous injection of theophylline-ethylenediamine (Euphyllin) produces a diuresis which progressively increases with increasing alkalinity. The action of purine diuretics cannot be ascribed to loss of water from serum proteins since the purines investigated do not lower the viscosity of serum-albumin until the p_H is raised to 9.
J. P.

Fate of Morphine in the Animal Body. I. Excretion of Morphine in Warm-blooded Animals. T. TAKAYANAGI (*Arch. Exp. Path. Pharm.*, 1924, **102**, 176—182).—Contrary to the findings of Faust (*ibid.*, 1900, **44**, 217), morphine is excreted almost wholly in the urine and but slightly in the fæces. It appears slowly in the former, and 2—3 days after administration its excretion reaches a maximum and then rapidly declines during the succeeding few days. In animals previously treated with morphine, the excretion of a subsequent dose is more rapid than that of the first dose.
J. P.

Fate of Morphine in the Animal Body. II. Destruction of Morphine in the Body of Habituated and Non-habituated Rats. T. TAKAYANAGI (*Arch. Exp. Path. Pharm.*, 1924, **102**, 183—187).—In confirmation of the observations of Rübsamen (*ibid.*, 1908, **59**, 227), rats become less susceptible to repeated doses of morphine. This is ascribed to an increased rate of destruction (and excretion, cf. preceding abstract) and an increased cell immunity to the alkaloid.
J. P.

Intensity of Action on Nerve-endings of various Substituted Quaternary Aliphatic Ammonium Bases. F. KÜLZ (*Arch. Exp. Path. Pharm.*, 1924, **102**, 283—288).—The paralysing action of the halides of various alkyl and other substituted quaternary ammonium bases and of phenyltrimethylammonium chloride on the isolated nerve-muscle preparation of the frog is in the inverse order of the solubilities of the corresponding perchlorates (cf. Hofmann, Höbold, and Quoos, A., 1912, i, 164), with the exception of glyceryltrimethylammonium chloride. A theoretical discussion is appended. J. P.

Specific Rôle of Calcium in the Formation of Thrombin. E. Wöhlisch and K. Paschkis (*Klin. Woch.*, 1923, **2**, 2319; from *Chem. Zentr.*, 1924, i, 1220).—Plasma from birds loses its coagulability with muscle extract after being dialysed against 1% sodium chloride solution. Coagulability is restored by addition of calcium. G. W. R.

Theory of the Action of Thrombin. E. Wöhlisch (*Klin. Woch.*, 1923, **2**, 1801—1802; from *Chem. Zentr.*, 1924, i, 1219—1220).—In opposition to the theory of Herzfeld and Klinger that thrombin acts by the removal of a stabilising adsorption layer from fibrinogen, the author holds that coagulation by thrombin is similar to spontaneous coagulation and that thrombin acts as a specific catalyst of the coagulation of fibrinogen. G. W. R.

Cholesterogenic Function of the Spleen. J. B. Abelous and L. C. Soula (*Compt. rend.*, 1924, **178**, 1850—1852).—The serum of a normal dog taken after the ingestion of fat and kept *in vitro* at the ordinary temperature increases in cholesterol content at the expense of the fatty acids present. In the case of dogs from which the spleen had been removed, the serum decreases in cholesterol content whilst the fatty acids and total lipoids increase. In the latter case, addition of extract of the spleen induces normal behaviour with the difference that neither total lipoids nor fatty acids decrease. The general conclusion is drawn that the spleen is of great importance in the metabolism of fats because of its cholesterogenic function. H. J. E.

Method for Preserving Micro-organisms. C. Truche (*Ann. Inst. Pasteur*, 1924, **38**, 516—519).—A modification of Ungermann's method for keeping cultures of pathogenic bacteria alive for considerable periods without sub-culturing is described. Tubes of Legroux's formalised serum, each covered with a layer of vaseline oil, are used. Many organisms such as meningococcus, gonococcus, cholera vibrio, etc., which are difficult to keep in the ordinary way without deterioration, have been preserved for periods from 4 months to 2 years. [Cf. *B.*, 1924, 761.] C. T. G.

Odour of Cultures of *Bacillus pyocyaneus*. C. Gessard (*Compt. rend.*, 1924, **178**, 1857—1859).—The odour produced by cultures of *B. pyocyaneus* in the usual media is also obtained when using tryptophan in a decoction of seed of *Lupinus albus*, but only to a slight extent when the former is replaced by other amino-acids. When tryptophan is the sole organic constituent of the medium, the characteristic odour is also obtained. H. J. E.

Anaërobic Bacteria. I. Growth and Biochemical Activities of *Bacillus botulinus*, *B. sporogenes*, and *B. tetani*. E. Wagner, C. C. Dozier, and K. F. Meyer (*J. Infect. Dis.*, 1924, **34**, 63—84).—*B. botulinus* and *B. sporogenes* show a similarity in ammonia and amino-acid nitrogen accumulation; with *B. tetani*, the former was more marked towards the end of the experiment, and the latter was smaller. *B. tetani*, but not the other bacteria, utilised practically all the creatinine present and produced a greater accumulation of volatile acids; equal amounts of non-volatile acids were formed in the three cases. Under the conditions employed, Bengston's *B. botulinus*, type *C* (*U.S. Pub. Health Rept.*, 1923, **38**, 340), showed little chemical activity. CHEMICAL ABSTRACTS.

Anaërobic Bacteria. II. Effect of Dextrose on the Biochemical Activities of *Bacillus botulinus*. C. C. DOZIER, E. WAGNER, and K. F. MEYER (*J. Infect. Dis.*, 1924, **34**, 85—102).—Dextrose did not exert any effect on the production of toxin, which harmonises with the suggestion that the toxin is an autolytic product. CHEMICAL ABSTRACTS.

Utilisation of Lævulosans by Organisms. H. COLIN and V. ESTIENNE (*Bull. Soc. Chim. biol.*, 1924, **6**, 431—435).—Sucrose, which is the chief and the most common source of lævulose, is utilised by micro-organisms with great facility, although lævulosans, which are richer in lævulose and are just as sensitive towards acids as sucrose, are utilised imperfectly owing to the incapability of micro-organisms to hydrolyse them. The moulds, which are well-known for the diversity of their diastatic secretions, are only capable of attacking them with difficulty. In this respect, they may be classed with gums, mucilages, and pectins, with which they have in common certain physical characteristics. These substances are, however, capable of being utilised by the plants which elaborate them. D. R. N.

Fermentation of Galactose by *Saccharomyces cerevisiæ*. N. L. SOHNGEN and C. COOLHAAS (*J. Bact.*, 1924, **9**, 131—141).—The presence of *S. cerevisiæ* in a liquid medium containing galactose gives the newly-formed cells the property of fermenting this sugar, owing to the appearance of a new enzyme. This galactose zymase is more resistant than dextrose zymase, and remains, under favourable conditions, as a residue which is active after the stopping of growth. A high temperature will destroy dextrose zymase and leave galactose zymase. CHEMICAL ABSTRACTS.

Fermentation of Rare Sugars by Plant Pathogenic Bacteria. F. A. WOLF (*J. Elisha Mitchell Sci. Soc.*, 1922, **38**, 12—13).—*Bacillus tabacum* and *B. angulatum*, from tobacco, form acid from dextrose and sucrose but not from glycerol and lactose; the former, but not the latter, also attacks mannitol and galactose. A similar specialisation obtains with *B. glycineum* and *B. sojæ*, from soja-bean. CHEMICAL ABSTRACTS.

Acids produced by Hæmolytic and Non-hæmolytic *Streptococci*. B. LANGWILL (*J. Bact.*, 1924, **9**, 79—94).—During the first 24 hours, the acid production, in a sucrose or lactose infusion broth, of non-hæmolytic *Streptococci* was nearly twice that of hæmolytic strains, but the eventual acidity produced was equal.

The non-volatile acid was almost entirely *dl*-lactic acid; the non-hæmolytic group produced formic, acetic, and a trace of butyric acids, whilst the hæmolytic group and *S. viridans* produced acetic and propionic acids, but not formic acid. CHEMICAL ABSTRACTS.

Bacterial Association. I. Production of Lactic Acid. H. B. SPEAKMAN and J. E. PHILLIPPS (*J. Bact.*, 1924, **9**, 183—198).—The characteristic production of large amounts of lactic acid by *Bacillus granulobacter pectinovorum* and *B. volutans* growing in association, in media containing carbohydrate, is due to a partial inhibition of the physiological processes of *B. granulobacter pectinovorum* by some factor produced in *B. volutans* cultures. The inhibitory factor is not characteristic of cultures of *B. volutans* grown for several generations in carbohydrate media. It is suggested that this substance may be a product of the nitrogen metabolism of *B. volutans* growing in media containing vegetable protein and only traces of carbohydrate. CHEMICAL ABSTRACTS.

Quantitative Action of Enzymes of Seven Specific Organisms on the Proteins of Milk and on Gelatin. E. H. PARFITT and G. SPITZER (*J. Bact.*, 1924, **9**, 123—130).—The amount of peptone produced by the enzymes of different organisms is approximately four times greater in gelatin than in milk. The rate of peptonisation of gelatin is practically constant, being about 0·2% per hour except for *Bacillus mesentericus*, in which case it is slower. The digestive period was the same for casein and egg-albumin. CHEMICAL ABSTRACTS.

Cystine in Bacterial Metabolism. J. GORDON (*J. Path. Bact.*, 1924, **27**, 123—124).—Organisms which form hydrogen sulphide from cystine, such as the colon–typhoid group and the anaërobes, can tolerate large concentrations of the substance. Exceptions are *Bacillus paratyphosus A*, and *B. dysenteriæ*, Flexner. Cystine probably improved the growth of anaërobes. The delicate organisms do not split cystine and are highly sensitive to it. Perhaps serum in media acts as a protective colloid against toxic concentrations of amino-acids in the medium. In order to exert its effect on an organism, cystine must be in solution. This was done with a small amount of gelatin. CHEMICAL ABSTRACTS.

Oxidation and Reduction by *Pneumococcus*. III. Reduction of Methylene-blue by Sterile Extracts of *Pneumococcus*. IV. Oxidation of Hæmotoxin in Sterile Extracts of *Pneumococcus*. V. Destruction of Oxyhæmoglobin by Sterile Extracts of *Pneumococcus*. O. T. AVERY and J. M. NEILL (*J. Exp. Med.*, 1924, **39**, 543—552, 745—755, 757—775).—III. Peroxide formation and methylene-blue reduction are believed to be functions of the same or closely-related systems.

IV. The destruction of hæmotoxin in extracts capable of undergoing autoxidation is probably due to a peroxide.

V. The mechanism of, and conditions for, the conversion of oxyhæmoglobin into methæmoglobin are discussed.

CHEMICAL ABSTRACTS.

Correlation of Citrate Utilisation by Members of the Colon–Aerogenes Group with other Differential Characteristics and with Habitat. S. A. Koser (*J. Bact.*, 1924, 9, 59—78).—*Bacillus coli* of fæcal origin is unable to utilise sodium or potassium citrate when supplied as the sole source of carbon, whereas the aerogenes–cloacæ group, which formed the largest section of soil cultures, all utilised citrate readily.

Chemical Abstracts.

Radioactivity and Nitrogen-fixing Bacteria. E. Kayser and H. Delaval (*Compt. rend.*, 1924, **179**, 110—112; cf. Stoklasa, A., 1913, i, 1421).—A radioactive uranium mineral (60% uranium oxide) is able to produce increased nitrogen fixation by various nitrogen-fixing bacteria. The bacteria which have been grown in media containing small quantities of the radioactive substance are more elongated and of greater mobility than the normal strain. The addition of 15 mg. of the radioactive mineral per litre of culture media produces a 67% increase in the amount of nitrogen fixed in 40 days at 26° in the case of *Azotobacter chroococcum*, 250% increase with "Azotobacter de la Comore," and 35% with *A. agile*, whilst for the addition of 30 mg. per litre the corresponding increases are 78%, 506%, and 56%. It is suggested that by the production of successive generations of the bacteria in the presence of an optimum quantity of the radioactive substance, a strain with much greater power of nitrogen fixation in liquid media or in the soil may be obtained.

J. W. B.

Decomposition Products of Spore-bearing Bacilli in Heated Milk. H. Lisk (*J. Bact.*, 1924, 9, 1—12).—Aërobic spore-bearing bacilli showed a progressive increase in ammonia formation with a similar but larger increase in amino-nitrogen. Formation of indole and hydrogen sulphide, but not of mercaptan, was sometimes observed.

Chemical Abstracts.

Mode of Action of Bismuth Derivatives in Spirillosis and Trypanosomiasis. C. Levaditi (*J. State Med.*, 1924, **32**, 62—81; cf. *Compt. rend.*, 1922, **176**, 1189).—The physiological action of bismuth appears to depend on its conversion into "bismoxyl" by a partly thermostable, colloidal, organic substance ("bismogene") in the cellular extracts. Contact between "bismogene" and a bismuth derivative gives rise to flocculation of protein colloids, accompanied by spirillicidal and trypanocidal activity; "bismoxyl," composed of bismuth and a protein flocculated colloidal complex, is relatively thermostable, and does not pass through porcelain filters. The bismuth content of the complex is not constant. Bismuth is a more effective spirillicidal agent than arsenic.

Chemical Abstracts.

Action of Potassium and Copper Dichromates on the Growth of *Phytophtora infestans*. A. and R. Sartory (*Compt. rend.*, 1924, **179**, 69—70).—Copper dichromate is twice as toxic as potassium dichromate to *P. infestans*.

T. H. P.

Hormone of the Placenta and of the Corpus Luteum and the Lipoids of the Corpus Luteum. O. O. Fellner (*Biochem. Z.*, 1924, **147**, 185—186).—A claim of priority in relation to the citation by Fränkel and Fonda (A., 1923, i, 1257) of Hermann's work on the placental hormone (*Zentr. allgem. Pathol.*, 1912, **23**). The author states that the hormone does not survive the vacuum distillation employed by Fränkel and Fonda as a method of isolation, but that it is readily purified by extraction with 75% alcohol, in which the accompanying impurities are insoluble. J. P.

Catalytic Action of Minute Amounts of Copper in the Destruction of Antiscorbutic Vitamin in Milk. A. F. Hess and M. Weinstock (*J. Amer. Med. Assoc.*, 1924, **82**, 952—956).—Antiscorbutic vitamin is readily destroyed by oxidation, particularly when heated, and in presence of small quantities of copper. Vitamin-*A* is also very sensitive to the destructive effect of oxidation. The amounts of copper concerned are considerably less than those showing a toxic effect. Chemical Abstracts.

Presence of Insulin-like Substance in Gastric and Duodenal Mucosa, and its Relation to Gastric Secretion. A. C. Ivy and N. F. Fisher (*Amer. J. Physiol.*, 1924, **67**, 445—450).—Using Fisher's method (*J. Amer. Med. Assoc.*, 1923, **81**, 920), a substance was obtained from the gastric and duodenal mucosa of the hog which produced an insulin-like effect in a diabetic dog. The method also extracts gastric secretin which, however, is not precipitated with insulin by half-saturation of an acid aqueous solution with ammonium sulphate. Chemical Abstracts.

Preparation of Insulin. T. B. Robertson and A. B. Anderson (*Med. J. Australia*, 1923, **2**, 189—191).—Four-fifths of the water contained in the extract containing 50% of ethyl alcohol is removed by means of anhydrous sodium sulphate.

Chemical Abstracts.

Influence of Insulin on Normal Metabolism in Man. C. H. Kellaway and T. A. Hughes (*Brit. Med. J.*, 1923, I, 710—711).—The results afford evidence of the combustion of dextrose, and of the transformation of dextrose into a complex poorer in oxygen.

Chemical Abstracts.

Factors Influencing the Production of Insulin. F. G. Banting and S. Gairns (*Amer. J. Physiol.*, 1924, **68**, 24—30).—High blood-sugar acts as a stimulus to the normal pancreas leading to the production of insulin adequate to reduce the blood-sugar to its normal level. Chemical Abstracts.

Insulin-like Compounds. I. T. Brugsch and H. Horsters (*Biochem. Z.*, 1924, **147**, 150—162).—An investigation by the blood-sugar test of substances, resembling insulin either physico-chemically or physiologically, isolated from various organs, by processes used in preparing the pancreatic hormone. Such substances are called "raw insulin" irrespective of their action on the blood-sugar. Thyroid extract and extract of epithelial material had practically no effect; suprarenal material gave results complicated by the presence of adrenaline; liver extracts caused a slight increase in blood-sugar; spleen extract produced a very slight and temporary fall. The human placenta yielded a "raw insulin," resembling that of the pancreas in physical and chemical properties, which caused a slight fall of blood-sugar. Alcoholic placental extracts proved very toxic to rabbits, producing spasms followed by death. Yeast yielded an "insulin" which is thought to differ from that of the pancreas. Sodium hydrogen phosphate and phosphite depressed the blood-sugar; an organic phosphorus compound (tonophosphan) had no effect; atophan and atoxyl produced increases in blood-sugar.

J. P.

Reaction of Living Protoplasm. R. SCHAEDE (*Ber. deut. bot. Ges.*, 1924, **42**, 219—224).—The plasma of the bulb scales of the onion absorbs methyl-red strongly. Small pieces were floated on an aqueous solution of methyl-red (0·004%) rendered just definitely acid and observed under the microscope. Within 5 to 10 minutes, the plasma of the upper epidermis was definitely coloured yellow, followed later by the plasma of the under epidermis. The cell-sap was strongly coloured red. Various organic and mineral acids were used for the preliminary acidification, and it was shown that neither the methyl-red nor the acids at the concentration used were poisonous to the plasma. Dead plasma under the same conditions is coloured red. Methyl-red therefore indicates that living plasma is alkaline in reaction.

C. T. G.

Mechanism of Photosynthesis. J. PEKLO (*Chem. News*, 1924, **129**, 90—94).—Experiments on the poisoning of living cells by various compounds support Willstätter's theory of the formation of a formaldehyde–peroxide complex as an intermediate product of photosynthesis.

A. A. E.

Absorption of Ions from the Soil through the Root System of Plants. J. STOKLASA (*Ber. deut. bot. Ges.*, 1924, **42**, 183—191).—Determinations are recorded of (1) the p_H of the sap in the roots of various cultivated plants, (2) the amount of carbon dioxide excreted per unit weight of the roots, (3) the numbers of bacteria in the soil in the neighbourhood of the roots, and (4) the amount of carbon dioxide respired per unit weight of the soil by the bacteria present. Contrary to the results of other workers, the hydrogen-ion concentration of the sap of the roots of plants grown in normally aërated soil was in no case found to be sufficiently high to account for the absorption of mineral constituents from the soil. The p_H figures varied only from 6·2 for buckwheat to 6·9 or 7·0 for wheat, barley, and potatoes. The amount of carbon dioxide excreted by the roots varied with different plants, but had no relation to the p_H of the sap. By growing plants in an artificial soil under sterile conditions and supplied with nitrogen in the form of ammonium salts, it was shown that the various species used possessed characteristic powers of preferential absorption of anions or cations, *e.g.*, cereals and buckwheat take up anions (phosphate) more readily than cations (potash), whilst beet and potatoes absorb more cations than anions. The yield from such cultures was much increased on inoculation with active bacteria from soil surrounding the roots of the same species of plant, indicating the important part played by bacteria in the absorption of mineral materials by the roots. The number of bacteria found in the neighbourhood of the roots is different for different species of plants grown in the same soil; and these differences are reflected in the amount of carbon dioxide respired by the soil. No appreciable differences were noticed in the p_H of the soil near the roots of the various plants. It is concluded that the absorption of difficultly soluble mineral nutrients by the root system of plants is brought about entirely by the action of carbon dioxide excreted by the roots and by carbon dioxide and organic acids produced by bacteria. C. T. G.

Occurrence of Inulin in the Leaves of *Marcgraviaceæ*. H. Melchior (*Ber. deut. bot. Ges.*, 1924, **42**, 198—204).—The cells of certain small swellings on the leaves of dried specimens of *Marcgravia macroscypha* from S. America were found to be filled with inulin. No starch was present in the leaf. The localisation of the inulin in special areas was probably due to the preliminary preservation of the specimens in alcohol. Inulin was also recognised in the fresh leaves of other species of *Marcgravia*, and again no starch was present. Experiments indicated that in plants of this genus inulin takes the place of starch as a primary product of assimilation. C. T. G.

Chemical Composition of the Green Fruit of Vanilla and Mode of Formation of the Perfume of Vanilla. A. Goris (*Compt. rend.*, 1924, **179**, 70—72).—Green vanilla fruit contains three glucosides: glucovanillin, which has been isolated; glucovanillic alcohol, which is characterised by the formation of vanillic alcohol on hydrolysis; and a glucoside, not yet isolated, but yielding, on hydrolysis, an ester having the odour of vanilla which gives a crystalline acid and an alcohol when treated with alcoholic sodium hydroxide. The glucovanillic alcohol probably gives rise to glucovanillin and then to vanillin, on oxidation. T. H. P.

Composition of the Turpentine Oils from *P. Laricio Austriaca* and *P. Laricio* of Spain. G. Dupont and M. Barraud (*Bull. Soc. chim.*, 1924, [iv], **35**, 784—792).—Turpentine oil obtained from *P. Laricio Austriaca* consists of 96% of *l*-pinene, about 1% of a dextrorotatory hydrocarbon, *d*-limonene (?), 1% of a sesquiterpene (hydrobromide, m. p. 115—115·5°), and 2% of esters and oxidation products. The turpentine oil obtained from the *P. Laricio* of Spain contains about 90% of *l*-pinene, 4% of *l*-limonene, 1·5% of a sesquiterpene, and 4·5% of oxidation and other products. The pinene obtained from the Spanish turpentine has a lower rotatory power than that from *P. Laricio Austriaca*. The two sesquiterpenes are not identical, since their hydrobromides have different melting points, although both terpenes with acetic anhydride, or acetic acid, and sulphuric acid give similar colour reactions. The higher-boiling fractions of both essences contain a strongly dextrorotatory constituent. R. B.

Elementary Composition of the Corn [Maize] Plant. W. L. Latshaw and E. C. Miller (*J. Agric. Res.*, 1924, **27**, 845—860).—Five Pride of Saline maize plants have been analysed at a stage when it could be assumed that the maximum amount of minerals had been removed from the soil. The average dry weight was distributed as follows: leaves, 28·10%; stem, 24·02%; grain, 31·26%; cob, 9·37%; roots, 7·25%. Of the total dry weight approximately 4% was mineral, 1·47% nitrogen, and 94·34% consisted of carbon, hydrogen, and oxygen. The variation in the amount of the different elements and their removal from the soil is discussed. O. O.

Sulphur Content of the Tomato. R. S. Marsh (*Amer. Soc. Hort. Sci. Proc.*, 1922, **19**, 83—84).—An increase of the sulphur content occurs with advancing age of the tissue; a high sulphur content is associated with a low phosphorus content. It is suggested that sulphur may liberate phosphorus from the older tissue for translocation to the younger tissue. Phosphate-fertilised plants show a marked increase in sulphur and phosphorus content, particularly near the blossoms. Chemical Abstracts.

Carbohydrate Reserves of Young Apple Trees as influenced by Winter Storage. P. T. Blood (*Amer. Soc. Hort. Sci. Proc.*, 1922, **19**, 33—35).—The total carbohydrates, including hydrolysable material, are approximately equal in the autumn in the trunks, branches, and roots, but the roots contained 25% less reducing sugar and 3 times as much starch as the trunks and branches. In the spring, a marked reduction in the total carbohydrates was observed; sucrose was then practically absent from the branches and trunks. The effect of the conditions of storage on the magnitude of the changes is recorded.

Chemical Abstracts.

Effect of Ringing a Stem on the Upward Transfer of Nitrogen and Ash Constituents. O. F. Curtis (*Amer. J. Bot.*, 1923, **10**, 361—382).—Ringing twigs and small branches of peach and other trees, either in the spring before the leaves are formed or in the summer when the leaves are fully-developed, affects adversely the movement of nitrogen and ash constituents into the leaves above the ring. When a dressing of sodium nitrate was given immediately after ringing, the nitrogen and ash constituents of the leaves from unringed stems and of the stems themselves increased to a much greater extent than did those of the leaves and stem when ringed. Experiments on privet indicated that the reduced nitrogen content above a ring is not caused by a lowering of transpiration and is independent of its effect on the carbohydrate content. The data afford strong, although not conclusive, evidence that nutrients are carried chiefly in the phloem. C. T. G.

Course of Acidity changes during the Growth Period of Wheat with Special Reference to Stem Rust Resistance. A. M. Hurd (*J. Agric. Res.*, 1924, **27**, 725—735).—Examination of the expressed juice of a number of varieties of wheat plants showed a general sequence of acidity changes through the period of growth. There was an initial decrease in titratable acidity during the first 2—6 weeks, followed by a period of low acidity which was maintained until the plants began to mature. From this time, the acidity increased fairly regularly to the ripening stage. The hydrogen-ion concentration did not show markedly the initial decrease, but rose considerably during the later stages of the plants' development. External conditions affected both hydrogen-ion concentration and titratable acidity. No correlation was apparent between acidity and susceptibility to stem rust, and resistant varieties showed the same sequence of acidity changes as non-resistant ones. A. G. P.

Daily Variation of the Carbohydrates in the Leaves of Corn [Maize] and the Sorghums. E. C. Miller (*J. Agric. Res.*, 1924, **27**, 785—807).—Portions of the leaves of maize and sorghum plants were examined at 2-hourly periods. The amount of dry matter per unit leaf area was always greater in the sorghum than in the maize. From daylight until about 4 p.m. there was a steady increase and later a steady decline until the following daybreak. The amount of water in unit leaf area was always greater in maize, and seemed to become a limiting factor in the production of dry matter when reaching a minimum of 112 g. per sq. metre of leaf. No such limitation occurred in the case of sorghum. The quantity of sugars in the leaves was at a minimum at daybreak and reached a maximum at from midday to 5 p.m. The insoluble carbohydrates reached a maximum later than the sugars and did not decrease appreciably in quantity until after midnight, after which there was a steady decline till daybreak. Non-reducing sugars were usually predominant, increasing during the day and declining at night. Reducing sugars varied to a much smaller extent, and were present in irregular amounts at different times of the day. A. G. P.

Effect of Nitrate Applications on the Hydrocyanic Acid Content of Sorghum. R. M. Pinckney (*J. Agric. Res.*, 1924, **27**, 717—723).—Pot experiments with sorghum showed that nitrate additions to soil in which the plants were grown improved the size and colour of the plants and also increased their hydrocyanic acid content. The latter effect was roughly proportional to the dose of nitrate applied and continued beyond the stage when increased nitrate ceased to affect the size or colour of the plant. In general, lighter coloured plants contained less hydrocyanic acid than darker ones and more was present in the leaf than in the stems. The possibility of utilising sorghum as an indicator plant in soil-nitrogen experiments is noted. A. G. P.

Action of Dicyanodiamide and Guanylcarbamide Sulphate on Plant Growth. A. F. McGuinn (*Soil Sci.*, 1924, **17**, 487—500).—Pot and water culture experiments with dicyanodiamide and guanylcarbamide sulphate showed that neither of these substances retards seed germination when applied in small quantities. In large amounts, dicyanodiamide was slightly toxic and very stable in soil. Guanylcarbamide sulphate showed no toxicity and was slowly decomposed to ammonia. Small doses of dicyanodiamide inhibit nitrification, but guanylcarbamide sulphate exerts only a slightly retarding action. Neither substance affects ammonification or the numbers of bacteria and fungi in soil. Urea has a fertilising value approximately equal to that of sodium nitrate, and its value does not diminish if 10% of its nitrogen is in the form of dicyanodiamide and guanylcarbamide sulphate. A. G. P.

Influence of Silica, Lime, and Soil Reaction on the Availability of Phosphates in Highly Ferruginous Soils. W. T. McGeorge (*Soil Sci.*, 1924, **17**, 463—468).—In a number of Hawaiian sugar-cane soils examined, high phosphate availability—as determined by extraction with 1% citric acid—was generally accompanied by high silica availability. Response to phosphate fertilisers was usually more marked in soils of low p_H value and those having smaller proportions of easily soluble calcium salts (carbonate, sulphate, and silicate). Relationships were traced between available phosphate and silicate, reaction, and soluble calcium, and the phosphate content of the cane juice. A. G. P.

Influence of Varying Ratios of Phosphoric Acid and Potash on Crop Yield and Nitrogen Recovery. A. W. Blair and A. L. Prince (*Soil Sci.*, 1924, **17**, 327—330).—A continuation of earlier work (cf. Lipman and Blair, *N.J. Agr. Expt. Sta.*, 44th *Ann. Rept.*, 1923). Maize was grown in cylinders, with fertilisers applied in various ratios, and harvested green as a forage crop. A ratio of 1 : 2 for nitrogen and phosphoric acid gave somewhat better yields than a ratio of 1 : 1 or 1 : 3. The form in which the nitrogen was used did not affect the percentage of nitrogen in the dry matter, but it influenced the yield and hence the nitrogen recovered in the crop. The recovery was on an average 43% from sodium nitrate, about 30% from ammonium sulphate, and just over 20% from dried blood. The amount of phosphoric acid in the fertiliser did not influence the percentage of nitrogen in the dry matter. C. T. G.

Mutual Effects on Soil and Plant Induced by Added Solutes. J. S. Burd and J. C. Martin (*Calif. Agr. Exp. Sta. Tech. Paper*, 1923, No. 13).—Treatment of soil with solutions of salts causes a substantial increase in water-extractable materials. The changes are ascribed to added solutes, chemical replacements of solid material, fixation by the solid phase, and increased solubility of solid material in the new soil solution. Addition of nitrate did not prevent the practical disappearance of that ion at the height of the growing season. Some irregular results are ascribed to the defects of water-extraction as a measure of the soil solution, or to the influence of changed concentrations of other constituents on the absorption of a given element by the plant. CHEMICAL ABSTRACTS.

Nitrification in Sudan Soils. F. J. MARTIN and R. E. MASSEY (*Wellcome Trop. Res. Lab., Khartoum, Chem. Sect. Publ.*, 1923, No. 29, 29 pp.).—In field experiments on irrigated soils at Shambat it was found that nitrates accumulated in considerable quantities in the tops of the ridges in irrigated land and in land carrying cotton. The nitrates disappeared from land in dry fallow. The accumulation of nitrate was ascribed to nitrogen fixation, and not to concentration of the soil solution by evaporation, since other soluble salts were washed down and tended to accumulate in the lower subsoil. The amount of nitrate in the surface of the ridge was many times greater than that in the furrows or the subsoil. It is suggested that this accumulated nitrate is not available for the crop. Flooding of the ridges in order to wash the nitrate into the soil was tried with some success. Ammonium sulphate gave the greatest crop increases for wheat and cotton when applied 6 to 8 weeks after sowing. E. M. C.

Nitrification. V. Mechanism of Ammonia Oxidation. A. BONAZZI (*J. Bact.*, 1923, **8**, 343—363).—Using an active form of *Nitrosococcus*, grown in Omeliansky culture solution, it was found that three atoms of oxygen were utilised by the organisms for each atom of nitrogen oxidised. The bacterium is able to cause the breakdown of hydrogen peroxide; but no peroxide-oxygen could be detected in the cultures. The changes undergone by the iron present in the nitrifying cultures were studied, and it is suggested that the iron acts as an oxygen carrier forming an intermediate ferrous oxide–peroxide from which the bacterial cells are able to obtain active oxygen. Thus, in the actual process of ammonia oxidation, iron plays the part of a peroxide and activates the inert oxygen of the air. The mechanism itself appears to be intracellular.

The presence of ammonium iodide had no harmful effect on the process of ammonia oxidation and no appreciable oxidation of the iodine to iodate was observed. C. T. G.

Chemical Factors in Denitrification. G. J. FOWLER and Y. N. KOTWAL (*J. Indian Inst. Sci.*, 1924, **7**, 29—37).—The stability of dilute solutions of ammonium nitrite under conditions likely to occur in sewage purification is investigated; and it is concluded that any loss of gaseous nitrogen in the operations of agriculture and sewage purification due to purely chemical causes is negligible. [Cf. *B.*, 1924, 728.] C. T. G.

Microbiological Analysis of Soil as an Index of Soil Fertility. IX. Nitrogen Fixation and Mannitol Decomposition. S. A. WAKSMAN and P. D. KARUNAKAR (*Soil Sci.*, 1924, **17**, 379—393; cf. *B.*, 1924, 106, 143, 394).—The nitrogen-fixing powers or mannitol-decomposing powers of soils from several experimental plots have been compared by four methods. The importance of phosphorus for the nitrogen-fixing organisms makes it possible to obtain in this way an indication of the amount of available phosphorus in the soil. The determination of the increase in total nitrogen following the addition of mannitol to the soil is untrustworthy owing to the lack of sensitiveness in the determination of total nitrogen. The increase of total nitrogen in a standard mannitol solution after inoculation with the soil sample and incubation serves as an index of the nitrogen-fixing flora of the soil and to some extent of the microbiological condition of the soil. The nitrogen fixation in a sterilised mixture of mannitol solution and soil, after inoculation with *Azotobacter* and incubation, can serve as an index of the available phosphate in the soil. Christensen's method of incubating the soil with mannitol and determining at intervals of 5 days the residual soluble organic matter, by oxidation with potassium permanganate, can serve as an index of the nitrogen-fixing flora and of the amount of phosphorus available in the soil. E. M. C.

Value of Soil Analysis when Limited to an Intensive Single Cropping System. W. T. McGeorge (*Soil Sci.*, 1924, **17**, 457—462).—The value of weak acid solvents, notably 1% citric acid, in determining the availability of potash and phosphate in sugar-cane soils is discussed. Under these limited conditions, the citric acid extract proved of considerable value in arriving at fertiliser requirements. Certain general relationships between availability and soil type are noted. A. G. P.

Intensity of Assimilation of Atmospheric Nitrogen by Forest Soils. A. Němec and K. Kvapil (*Bull. Soc. Chim. biol.*, 1924, **6**, 515—520; cf. *Compt. rend.*, 1923, **176**, 260).—A comparison of the amounts of nitrogen fixed under similar conditions in the presence of samples of both the humus and the lower mineral soil, from forests of various types and with different species of trees. G. M. B.

Sulphofication in Pure and Mixed Cultures, with Special Reference to Sulphate Production, Hydrogen-ion Concentration, and Nitrification. H. D. Brown (*J. Amer. Soc. Agron.*, 1923, **15**, 350—382).—No nitrogen was lost from soil in which large amounts of sulphur were oxidised. A close inter-relation existed between sulphofication, nitrification, and soil reaction. With the oxidation of sulphur, the hydrogen-ion concentration increased and nitrification was depressed. Liming increased both sulphofication and nitrification. E. M. C.

Toxic Organic Soil Constituents and the Influence of Oxidation. O. Schreiner (*J. Amer. Soc. Agron.*, 1923, **15**, 270—276).—The author reviews earlier work on the isolation from unproductive soils of harmful substances, such as picolinecarboxylic acid, dihydroxystearic acid, oxalic acid, salicylaldehyde, and vanillin. Toxic substances, especially aldehydes, are formed under conditions of imperfect aëration and oxidation. Such infertile soils are improved by the changed biochemical processes resulting from drainage, liming, rotations, green manuring, and fertilisation. E. M. C.

Organic Chemistry.

Methylethyl*iso*propylmethane and Di*iso*propylmethane. G. CHAVANNE and H. DE GRAEF (*Bull. Soc. chim. Belg.*, 1924, **33**, 366—375).—Methylethyl*iso*propyl carbinol [βγ-dimethylpentan-γ-ol], prepared by the action of magnesium *iso*propyl iodide on methyl ethyl ketone, and of magnesium ethyl bromide on methyl *iso*propyl ketone, has b. p. 42—43°/11 mm., 139·4—139·9°/760 mm. (slight decomp.), d_4^{15} 0·8445, n_D^{20} 1·4280. It is converted by *p*-toluenesulphonic acid into two isomeric dimethylpentenes, probably βγ-dimethyl-Δ^{β}-pentene and βγ-dimethyl-Δ^{γ}-pentene, b. p. 92° and 96—97° respectively, which are catalytically reduced in acetic acid to *methylethyl*iso*propylmethane* [*βγ-dimethylpentane*], b. p. 89·9—90·1°/760 mm., d_4^{15} 0·6991, d_4^{20} 0·6950, n_D^{20} 1·3918, separation point from aniline, 68·1±0·1°.

*iso*Butyl bromide is best prepared by the action of gaseous hydrogen bromide on cold *iso*butyl alcohol, the yield being 80%. Dimethyl*iso*butyl carbinol [βδ-dimethylpentan-β-ol], obtained by the action of magnesium *iso*butyl bromide on acetone, has b. p. 42—43°/11 mm., 132·8—133·4°/760 mm. (slight decomp.), d_4^{15} 0·8168, n_D^{20} 1·4172. The carbinol when dehydrated with *p*-toluenesulphonic acid gives dimethyl*iso*propylethylene [βδ-dimethyl-Δ^{β}-pentene], b. p. 83·1—83·3°/760 mm., d_4^{15} 0·6994, n_D^{20} 1·4016, the constitution of which is confirmed by oxidation with chromic acid to acetone and *iso*butyric acid. Reduction in the presence of platinum converts it into di*iso*propylmethane [βδ-dimethylpentane], b. p. 80·7—80·9°/760 mm., m. p. —119·4°, d_4^{15} 0·6769, n_D^{20} 1·3814, separation point from aniline, 78·6±0·1°. F. G. M.

Pyrogenic Dissociation of Hexadecene. H. GAULT and Y. ALTCHIDJIAN (*Compt. rend.*, 1924, **178**, 2092—2095).—The decomposition products consist of hydrogen, paraffins, and ethylenic hydrocarbons. The percentage of the last-named increases with temperature to a maximum of 67—68; further increase in temperature brings about a decrease in this yield. There is a corresponding minimum point for paraffins. The percentage of hydrogen increases slowly with rise of temperature. The authors have employed the apparatus previously described (Gault, Hessel, and Altchidjian, this vol., i, 701) and their results indicate that the size of the furnace used, whilst not altering the general results, shifts the temperature range over which they are obtained; *e.g.*, the maximum production of ethylenic hydrocarbons occurs at 570° with a 64 cm. furnace but at 685° with one of 16 cm. H. J. E.

Pyrogenic Dissociation of Hexadecane. H. GAULT and F. A. HESSEL (*Compt. rend.*, 1924, **179**, 171—173; cf. this vol., i, 701).—The pyrogenic decomposition of hexadecane at various temperatures and in furnaces of various lengths has been investigated. The formation of saturated hydrocarbons and of hydrogen in the gaseous products increased and that of unsaturated hydrocarbons decreased with increase of temperature from 600° to 815°; acetylene was detected in the products at 615° and in some cases at lower temperatures. Figures are given for the iodine absorption, density, and refractive index of the liquid products; except in one instance, these contained no aromatic hydrocarbons when tested by the solubility in methyl sulphate. F. G. M.

Catalytic Activation of Ethylene by an Organo-nickelic Compound. A. Job and R. Reich (*Compt. rend.*, 1924, **179**, 330—332).—On addition of successive small quantities of pure, powdered nickel chloride to an ethereal solution of magnesium phenyl bromide in the presence of pure, dry ethylene (the temperature being maintained strictly at 6°) the gas is rapidly absorbed, the rate being proportional, not to the amount of nickel chloride added, but to the quantity of the magnesium phenyl bromide employed. By the action of water on the very complex solution obtained, the main product is ethane, mixed with smaller quantities of liquid hydrocarbons, ethylbenzene, styrene, diphenyl, and some hydrocarbons of b. p. above 270°. The action of carbon dioxide yields a mixture of acids, among which formic, propionic, and phenylpropionic acids are identified. The catalyst is probably an organonickelic compound, the magnesium acting as the acceptor.
J. W. B.

Tautomerism of Dyads. II. Acetylene and its Halogen Derivatives. (Mrs.) E. H. Ingold (*J. Chem. Soc.*, 1924, **125**, 1528—1537).—The presence of small proportions of *iso*acetylene, $CH_2:C$, in acetylene is indicated by the thermodynamic method for the detection of tautomeric equilibria in very mobile systems (T., 1922, **121**, 1604) and by the formation of keten when the gas is very cautiously oxidised.

Chloroacetylene exists in two phases at the ordinary temperature, since α-chloro-ββ-di-iodoethylene is produced by passing the gas into a solution of iodine in benzene, whereas exposure of the gas, mixed with nitrogen, to bright light results in the isolation of *s*-trichlorobenzene. Further, the action of hypobromous acid leads to the formation of chloroacetic acid and chlorodibromoacetaldehyde, one derived from each of the two isomerides originally in equilibrium. Bromoacetylene also displays this dual chemical character. The dihalogen-acetylenes show no tendency to pass into halogenated benzenes; all the evidence supports the *iso*acetylene structure, and no fact is known which needs an assumption of the structure CBr:CBr. A. C.

Explosion of Acetylene and Nitrogen. III. Effect of the Addition of Oxygen on the Production of Hydrocyanic Acid. W. E. Garner and S. W. Saunders (*J. Chem. Soc.*, 1924, **125**, 1634—1641; cf. T., 1921, **119**, 1903; 1922, **121**, 1729).—The relation $K_1^{\text{II}}=[\text{HCN}]/[\text{C}][\text{N}_2]^{0\cdot37}$, which gives constant values for explosive mixtures of nitrogen and acetylene alone and when admixed with helium or hydrogen, no longer holds when oxygen is present. The production of hydrocyanic acid in explosive mixtures of acetylene, nitrogen, and oxygen, in which the content of nitrogen is kept constant at about 22% and the proportions of oxygen and acetylene are varied, increases with the proportion of oxygen, reaches a maximum in mixtures containing about 37% of oxygen, and then falls to zero. If the ratio of oxygen to acetylene exceeds 1 : 1, no hydrocyanic acid is found amongst the products; with mixtures richer in oxygen, appreciable amounts of carbon are not liberated at the temperature of the explosion and hence hydrocyanic acid cannot be formed. C. J. S.

Transformation of Acetylenic Hydrocarbons by means of Sodamide. BOURGUEL (*Compt. rend.*, 1924, **178**, 1984—1986; cf. Meunier and Desparmet, this vol., i, 701).—The action of sodamide at 110° on acetylenic hydrocarbons of the type $CR\vdots CMe$ results in the quantitative formation of the sodium derivatives of hydrocarbons, $CH_2R\cdot C\vdots CH$, with the evolution of an equimolecular quantity of ammonia. The action is more rapid than when sodium alone is used (cf. Faworsky, A., 1888, 1168), and none of the hydrocarbon is reduced. A similar transformation from $CR\vdots CEt$ into $CH_2R\cdot CH_2\cdot C\vdots CH$ occurs, but the reaction is much slower.
H. J. E.

Decomposition of Ethylene Bromide by Potassium and Sodium Iodide Solutions. T. S. PATTERSON and J. ROBERTSON (*J. Chem. Soc.*, 1924, **125**, 1526—1527).—Ethylene is evolved and iodine is liberated when mixtures of potassium iodide, water, and ethylene bromide are gently boiled. S. B.

Preparation of αα-Dichloro-β-bromoethylene. H. VAN DE WALLE (*Bull. Acad. Roy. Belg.*, 1924, [v], **10**, 94—108).—This compound (cf. Denzel, A., 1879, 368) may be prepared according to the scheme: $CH_2Cl\cdot CH_2Cl \longrightarrow CH_2{:}CHCl \longrightarrow CH_2Cl\cdot CHCl_2 \longrightarrow CH_2{:}CCl_2 \longrightarrow CH_2Br\cdot CCl_2Br \longrightarrow CHBr{:}CCl_2$. Repetition of the procedure given by Mouneyrat (A., 1899, i, 470) failed to yield *as.*-tetrachloroethane, but treatment of αβ-dichloroethane with alcoholic potassium hydroxide gives chloroethylene, which is converted by passage through cooled antimony pentachloride into ααβ-trichloroethane. Treatment of the latter with alcoholic potassium hydroxide in a current of nitrogen yields αα-dichloroethylene, which is readily brominated to αα-dichloro-αβ-dibromoethane, b. p. 175° (decomp.), 65°/13 mm., 70°/18 mm., m. p. −66·85°, d_4^{15} 2·2695, n_D^{15} 1·55930. Treatment with alcoholic potassium hydroxide solution then forms αα-dichloro-β-bromoethylene, b. p. 107—108°, m. p. −88·5°, d_4^{15} 1·9053, n_D^{15} 1·52028, which yields with alcohol an azeotropic mixture, b. p. 77·25°, containing 60·5% of alcohol. αα-Dichloro-αββ-tribromoethane, obtained by addition of bromine to the preceding compound (cf. Städel, A., 1879, 368; Denzel, *loc. cit.*), has b. p. 210° (decomp.), 106°/16 mm., m. p. 16·80°, d_4^{15} 2·6315, n_D^{20} 1·60035. αβ-Dichloro-ααβ-tribromoethane (cf. Swarts, A., 1899, i, 725) has b. p. 210° (decomp.), 112°/16 mm.,

m. p. 5·95°, d_4^{15} 2·6346, n_D^{15} 1·60846. The melting-point curve for mixtures of these two isomerides has a minimum at 4·20°, the crystalline phases being solid solutions having a gap between 80% and 100% of αβ-dichloro-ααβ-tribromoethane. T. H. P.

Action of Light on Solutions of certain Organic Substances in Chloropicrin. A. PIUTTI and P. BADOLATO (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 475—479).—Investigation of the compounds formed when solutions in chloropicrin of acetic acid, ethyl succinate, methyl salicylate, toluene, naphthalene, phenol, ψ-cumene, or *o*-, *m*-, or *p*-xylene were exposed to light for several months showed that, although chloropicrin is stable in the dark, it decomposes in the light into products having a chlorinating, oxidising, or substituting action on the solute. In some instances, the nitro group underwent reduction to the ammonium group, which separated as chloride or oxalate. T. H. P.

Halogenation of *s*.-Dipotassium Tetranitroethane. L. HUNTER (*J. Chem. Soc.*, 1924, **125**, 1480—1484).—The action of chlorine on a solution of *s*.-dipotassium tetranitroethane and sodium acetate in water results in the precipitation of s.-*dichlorotetranitroethane*, $CCl(NO_2)_2{\cdot}CCl(NO_2)_2$, m. p. 107° after incipient decomposition at 60—65°. Boiling water causes it to decompose into carbon dioxide, oxides of nitrogen, hydrochloric acid, and dichlorodinitromethane. It shows the usual reactions of "positive" halogen, characteristic of the *gem*-halogen-nitroparaffins. With 50% potassium hydroxide solution it is reconverted into *s*.-dipotassium tetranitroethane. Potassium iodide solution gives the same result, iodine being precipitated. Vigorous reaction takes place with potassium cyanide: cyanogen chloride is evolved and a black powder separates, whilst the filtrate contains carbonate, nitrite, and chloride. ααβ-Tribromo-αββ-trinitroethane (cf. Scholl and Brenneisen, A., 1898, i, 345), when treated with potassium iodide, also gave *s*.-dipotassium tetranitroethane, the potassium nitrite formed by a side decomposition acting as nitrating agent. Attempts to prepare the bromine analogue of *s*.-dichlorotetranitromethane resulted in the formation of dibromodinitromethane, $CBr_2(NO_3)_2$. Although *s*.-dipotassium tetranitroethane is stable towards iodine as illustrated in the preparation of this salt from bromopicrin and potassium iodide (Hunter, T., 1923, **123**, 543), attempts to increase the yield by addition of potassium nitrite resulted in a diminished yield and production of *potassium iodonitromethane* as a by-product, orange leaflets, exploding at 154—156°, *silver* salt, explosion point 104—106°. Salts other than potassium nitrite failed to effect this change. A. C.

Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. V. Preparation of Primary Alcohols by Catalytic Hydrogenation of Aldehydes. W. H. CAROTHERS and R. ADAMS.—(See i, 968.)

Action of Aluminium Sulphide on certain Organic Compounds [Ethyl Alcohol]. G. R. LEVI and G. NATTA.—(See i, 952.)

Dehydration of Alcohol. The System: Water–Alcohol–Hydrocarbon–Potassium Carbonate. Equilibrium between the Three Liquid Phases. L. GAY, P. MION, and SERVIGNE (*Chim. et Ind.*, May 1924 [special number], 286—295).—The equilibrium between water, liquid hydrocarbons (both pure and mixed), alcohol, and potassium carbonate is theoretically examined, the general conclusions being confirmed experimentally. The amount of alcohol in the hydrocarbon layer is independent of the potassium carbonate concentration in the lower, aqueous layer, provided this concentration is below 30%. Potassium carbonate is not sufficiently soluble at 20° to render alcohol and hydrocarbon miscible at this temperature. A good dehydrating agent must, in aqueous solution, have negligible solubility in the hydrocarbon–alcohol mixture, or the alcohol must be practically insoluble in the solution of the dehydrating agent. A sufficiently concentrated potassium carbonate solution, containing about 45% of the salt, fulfils these conditions. S. K. T.

Rotatory Dispersive Power of Organic Compounds. XII. Octyl Alcohol and Octyl Oxalate. T. M. LOWRY and E. M. RICHARDS (*J. Chem. Soc.*, 1924, **125**, 1593—1597).—Determinations of the rotatory dispersion of *sec.*-octyl alcohol for 19 wave-lengths by the visual method and 6 other wave-lengths by the photographic method have shown that the results can be expressed by one term of Drude's equation. The dispersion of octyl oxalate over a range of 27 wave-lengths is more complex and can be expressed neither by the one-term equation nor by Biot's law, although the results approximate to the latter. C. J. S.

Trimethylethylglycerol [βδ-Dimethylhexane-βγδ-triol]. PASTUREAU and H. BERNARD (*Compt. rend.*, 1924, **179**, 181—184; cf. A., 1922, i, 717; 1923, i, 646).—Magnesium ethyl bromide reacts with the chlorohydrin of mesityl oxide to give *γ-chloro-βδ-dimethylhexane-βδ-diol*, m. p. 35—37°, b. p. 105—110°/5 mm., which, on treatment with potassium carbonate, gives *βδ-dimethylhexane-βγδ-triol*, m. p. *ca.* 75°. Magnesium ethyl bromide and mesityl oxide give *βδ-dimethyl-Δ^{β}-hexan-δ-ol*, b. p. 45—47°/9 mm., which reacts vigorously with hypoiodous acid; the resulting iodohydrin is too unstable to be isolated (cf. A., 1923, i, 891). F. G. M.

Ethers of Polysaccharides with Hydroxy-acids. J. K. CHOWDHURY (*Biochem. Z.*, 1924, **148**, 76—97).—By the action of chloroacetic acid on polysaccharides in the presence of concentrated aqueous sodium hydroxide, ethers are obtained which, when thoroughly dried, are insoluble in water and in organic solvents. In the case of the cellulose ethers of glycollic acid the preparation with the lowest content of acid had one molecular proportion of the latter to three glucose residues, whilst that with the highest acid content had three molecules in each glucose residue. By the action of phosphorus tri-iodide and water on the cellulose glycollic acid ethers, cellulose and glycollic acid were obtained. In the cases of starch and inulin the highest degrees of substitution attained were respectively 2 mols. and 2½ mols. of acid per glucose residue.

The more highly substituted derivatives form insoluble salts with the alkaline-earth metals, and may be separated from the less highly substituted compounds of which the corresponding salts are soluble in water. The monosubstituted cellulose derivative exists as a lactone, that of starch as a mixture of free acid and lactone. The partly substituted cellulose derivatives may be methylated by means of methyl sulphate and sodium hydroxide, the carboxyl groups of the acid residues undergoing a partial methylation. The resulting product is soluble in cold, but insoluble in hot water. In the case of starch the carboxyl group does not undergo esterification and the product, which is soluble in both cold and hot water, shows a combined acid and methoxyl content corresponding with a substitution of 2⅓ of the three available hydroxyl groups in each glucose residue. By the action of chloropropionic acid and sodium hydroxide on cellulose, lactic acid ethers were obtained in small yields, but the formation of similar products was not observed using chloro- and bromo-malonic acids. J. P.

Methylations. Hydrolysis of Methyl Sulphate. H. F. LEWIS, O'N. MASON, and R. MORGAN (*Ind. Eng. Chem.*, 1924, **16**, 811—812).—The reaction, $Me_2SO_4+H_2O=MeHSO_4+MeOH$, is complete within 3 mins. at 95° in mixtures of methyl sulphate and water containing from 0·5 to 75·0% of the former. The hydrolysis of the methyl hydrogen sulphate is considerably slower with concentrations of methyl sulphate up to 5%, thereafter increasing rapidly with increase in concentration of the latter, a mixture containing 75% of methyl sulphate being hydrolysed to the extent of 96% in 3 mins. In mixtures containing 1% of methyl sulphate, the presence of 1% of sulphuric or hydrochloric acid produces an initial decrease, and subsequent increase in the rate of hydrolysis as compared with water alone, these variations being less marked with 25% sulphuric acid. In mixtures containing 25% of methyl sulphate, the presence of any acid decreases the rate of hydrolysis, whilst in mixtures containing 1 or 25% of methyl sulphate, the presence of 25% of acetic acid affords almost complete resistance to hydrolysis of the methyl hydrogen sulphate. The hydrolysis is depressed by alkalis and salts, potassium hydroxide showing greater hydrolytic activity than sodium hydroxide with low concentrations of methyl sulphate, whilst potassium chloride is a stronger depressant than sodium chloride. F. G. W.

Autoxidation of Organic Sulphur Compounds. M. DELÉPINE (*Bull. Soc. chim. Belg.*, 1924, **33**, 339—365).—A lecture delivered before the Chemical Society of Belgium.

F. G. M.

Method of Preparing Sulphinones. L. BERT (*Compt. rend.*, 1924, **178**, 1826—1828).—*Di-n-butyl sulphite*, a colourless liquid, b. p. 230° (slight decomp.), 111°/15 mm., d^{14} 1·001, n_D^{14} 1·435, was prepared by the action of sulphur chloride on butyl alcohol at 100°. When 1 mol. is added to 2 mols. of an organo-magnesium compound of the type MgRX, the corresponding sulphinone R_2SO is obtained.

H. J. E.

Action of Diazo Salts on Methanesulphonamide. P. K. Dutt (*J. Chem. Soc.*, 1924, **125**, 1463—1465; cf. T., 1921, **119**, 2088).—Methanesulphonamide, m. p. 84—85°, was prepared by slowly dropping methyl sulphate into a mixture of a solution of sodium sulphite and boiling methyl alcohol and treating the sodium methanesulphonate (yield *ca.* 94%) successively with phosphoryl chloride and dry ammonia. When it is dissolved in sodium hydroxide and mixed with a solution of benzenediazonium chloride, a yellow solid appears which quickly decomposes and produces phenylazoimide. After the removal of the latter, the aqueous portion is treated with a second portion of benzenediazonium chloride equal to that first used, whereby the *compound*,

$$Me\cdot SO_2\cdot N\colon NPh,$$

yellow needles, m. p. 71—72° (decomp.), is produced. The *substance*, $Me\cdot SO_2\cdot N\colon N\cdot C_7H_7$, prepared similarly from *p*-toluenediazonium chloride, has m. p. 112—113° (decomp.). The interaction of toluene-ω-sulphonamide with benzenediazonium chloride gave a tarry product from which only phenylazoimide could be isolated. The stability of these diazoamines appears to depend on some influence at present unknown. A. C.

Thermal Decomposition of some Pure Metallic Acetates. W. Krönig (*Z. angew. Chem.*, 1924, **37**, 667—672).—The dried acetates of lithium, sodium, potassium, copper, magnesium, calcium, barium, lead, and manganese, when gradually heated to 500°, appear normally to break down directly into acetone, metal oxide, and carbon dioxide, the last two then combining to a greater or less extent. The best yield of acetone is given by lithium acetate, the residue being almost pure lithium carbonate. Sodium, potassium, calcium, and barium acetates also give a residue consisting essentially of metallic carbonate, but the distillate from the first two contains a large amount (37% and 52%, respectively) of an oily condensation product, insoluble in water. The decomposition of copper acetate resembles that of silver acetate, the residue comprising the metal (with a small quantity of oxide) and carbon, and the distillate nearly pure acetic acid. Magnesium and manganese acetates yield mainly the metallic oxide, acetone, and carbon dioxide. With lead acetate, the lead oxide first formed oxidises a portion of the acetone, and the residue consists of nearly pure lead. An examination of the thermal decomposition of zinc acetate was impossible owing to excessive sublimation. The yield of acetone from metallic acetates appears to be related to the basicity of the metal. W. T. K. B.

Hydrates in Aqueous Solution. II. Citrate, *d*-Tartrate, Acetate, and Oxalate Ions. R. Fricke and H. Schützdeller (*Z. anorg. Chem.*, 1924, **136**, 295—304).—Determinations of the viscosity, freezing point, and density of aqueous solutions of the neutral potassium salts of citric, *d*-tartaric, acetic, and oxalic acids of varying concentrations indicate that the anions, especially the first three, are strongly hydrated. Hofmeister's series of decreasing hydration—citrate, tartrate, sulphate, acetate—is true only if solutions of equimolar concentration are compared; it does not hold for solutions of equal normality. The molar depression of the freezing point of solutions of potassium oxalate or tartrate falls continuously with increasing dilution, whereas that of solutions of potassium citrate or acetate has a minimum value. Normal potassium citrate ($+H_2O$) has d_4^{18} 1·995 and fused potassium acetate d_4^{18} 1·519. A. R. P.

Marine Animal Oils. Identity of Phocenic and Valeric Acids. E. André (*Bull. Soc. chim.*, 1924, [iv], **35**, 857—868).—Phocenic acid, derived from dolphin's head or whale oil by hydrolysis, is shown to be identical with valeric acid. The author thus refutes the suggestions made both by Lewkowitsch ("Chemical Technology of Oils, Fats and Waxes," 5th ed., p. 152) and Fryer and Weston ("Technical Handbook of Oils, Fats and Waxes," 3rd ed., p. 37) that the oil consists of a mixture of the glycerides of *n*-butyric and hexoic acids. A. E. C.

Oil from *Mimusops Hexandra*: Rayan Oil. C. K. Patel (*J. Indian Inst. Sci.*, 1924, 7, 71—80).—Rayan seeds yield 24·6% of an edible oil which is equivalent to a yield of 47·2% on the kernels. The oil, $d_{15\cdot5}^{15\cdot5}$ 0·914, n_D^{60} 1·4528, saponification value 190, iodine value 65, has a faint odour, is nearly colourless, is readily refined by alkali, and is easily hydrolysed by castor-seed lipase. The curve relating iodine value with refractive index is exactly similar to those for mohua, cotton-seed, and cashew-kernel oils. The fatty acids obtained by hydrolysis are palmitic, stearic, and oleic, with very small amounts of lignoceric and linolic, and the unsaponifiable matter consists of a liquid with a high refractive index and a sterol, probably ergosterol. The oil also contains a small quantity of a bitter principle soluble in water, probably a saponin. P. M.

Dehydrogenating Action of Nickel–Copper Catalysts. G. Kita, T. Mazume, and K. Kino (*Chem. Umschau*, 1924, **31**, 165—167).—Catalysts were used containing 16·9% of Ni and 3·1% of Cu; 14·0% of Ni and 6·0% of Cu; and 10·5% of Ni and 9·5% of Cu on kaolin. Stearic acid at 300—310° does not undergo dehydrogenation, but ketonic decomposition takes place, the amount increasing with increase of copper in the catalyst. With herring oil, dehydrogenation of the fatty acid takes place at 200° and at 170° with those catalysts containing more copper, and hydrogenation with those containing only nickel or nickel and a little copper. The catalyst containing little copper shows slight dehydrogenation at 100°. The temperature of reduction of the catalyst has an important effect; that reduced at 340—350° shows some dehydrogenating activity even at 100°, but that reduced at 220—230° shows none at any of the temperatures employed. P. M.

Wool Fat. F. Grassow (*Biochem. Z.*, 1924, **148**, 61—75).—By hydrolysis of wool fat with *N*/2-potassium hydroxide, cerotic acid,

$C_{27}H_{54}O_2$, m. p. 78°, was obtained and identified by comparison, together with its derivatives (methyl, ethyl, and cholesteryl esters, amide, *anilide*, m. p. 97°) with a corresponding preparation from beeswax. The *menthyl* ester, m. p. 43—44°, and the *phenyl* ester, plates, m. p. 59°, are described. *Methyl* and *benzyl lanocerinates*, m. p. 79—80° and 80°, respectively, are also described. By the action of benzoyl chloride on the silver lanocerinate, the mixed *anhydride*, $C_{29}H_{57}(OH)_2 \cdot CO \cdot OBz$, m. p. 76°, was obtained.

J. P.

Decomposition of Animal Wax. A. MAILHE (*Compt. rend.*, 1924, **179**, 184—185).—A mixture of 300 g. of beeswax, m. p. 64°, and 50 g. of anhydrous magnesium chloride was cautiously heated. At the beginning of the reaction the gas evolved contained CO_2 39%, CO 25·5%, CH_4 9%, and H_2 26·5%. As the temperature rose to 500°, about 215 g. of distillate were collected, whilst a sample of the gas evolved contained CO_2 14·5%, CO 22·4%, olefines 23·5%, methane 17·4%, other paraffins 18%, and H_2 4·2%. The distillate, when freed from acids, had b. p. 55—350°, and contained paraffins, olefines, and an unidentified ketone, white needles, m. p. 53—54°. Zinc, calcium, and barium chlorides and metallic oxides gave similar results. F. G. M.

Action of Halogens on Unsaturated Aliphatic Compounds. J. J. CERDEIRAS (*Bull. Soc. chim.*, 1924, [iv], **35**, 902—904).—Wijs' reagent is 3—4 times more reactive than iodine in acetic acid solution towards olive and linseed oils, and 2—3 times as reactive towards oleic and linolenic acids. In each case, the reaction with Wijs' reagent is practically complete after 40 mins.

A. E. C.

Natural Soaps in Soja Bean. S. MURAMATSU (*J. Chem. Soc. Japan*, 1923, **44**, 1035—1049).—When powdered soja bean, after being freed from fats and free acids, is extracted with warm alcohol (80%), the amount of soaps dissolved in the case of different species of the bean (even when unripe) is 1·44—1·86% of the dried bean. The total acids of the soap are composed of fatty and hydroxy-acids. The mixed fatty acids have acid value 177·1; mean mol. wt. 316·9. They can be separated into liquid acids, m. p. 38° (29·31% of the total organic acid), and solid acids, m. p. 55° (4·63%). The purified hydroxy-acid, $C_{34}H_{68}O_{17}$, white crystals, m. p. 224°, is named *hispidic acid*. It gives a *hexa-acetyl* derivative, m. p. 155°. The alkali salts of hispidic acid easily give a viscous, aqueous solution, which has marked foam-forming and detergent powers. K. K.

Relation between the Iodine Values and Refractive Indices of Hardened Oils. II. H. E. WATSON and J. J. SUDBOROUGH (*J. Indian Inst. Sci.*, 1924, 7, 81—95).—Iodine values and refractive indices for oils of different degrees of hydrogenation are recorded for argemone, English mustard, Indian rape, cashew kernel, soja bean, poppy-seed, rayan, olive, seal, and cod-liver oils. Rocket, mustard, and rape oils have higher refractive indices for a given iodine value than all the other oils examined except castor and argemone oils, this being attributed to the presence of glycerides of erucic acid. The high ratio of refractive index to iodine value for argemone oil is not due to glycerides of erucic acid, but to diglycerides and glycerides of hydroxy-acids. The refractive index for completely hardened olive oil (n_D^{60} 1·4463) agrees very closely with that of the purest tristearin (1·4462). Most of the curves are approximately parallel, but that for seal oil is exceptional and crosses most of the others. P. M.

Theory of Polymerisation in Fatty Oils. II. R. S. MORRELL (*J. Oil and Colour Chem. Assoc.*, 1924, **7**, 153—160).—The degree of polymerisation of fatty oils is not accurately indicated by the determination of the iodine value on account of the depolymerising action of some of the components of Wijs' solution. The molecular weight of these oils cannot be satisfactorily determined with benzene as a solvent, as esters show a tendency to combine with the solvent, and association occurs if acids be present. The polymerisation of linseed oil may be extramolecular as well as intramolecular, and it must be viewed from a colloidal as well as from a strictly chemical aspect. The ethyl esters derived from linseed and tung oils show a greater gain in weight in "drying" than do the glycerides, but the resulting films are liquid, and not solid as in the latter case, where polymerisation followed by gelation takes place. There is absorption of oxygen in both cases. P. M.

Equilibrium between Lactic Acid and its Anhydrides. G. I. THURMOND and G. EDGAR (*Ind. Eng. Chem.*, 1924, **16**, 823—826).—In a mixture of lactic acid, lactic anhydride, and lactide, the free acid is determined by direct titration of an alcoholic solution of the mixture with 0·3*N*-sodium hydroxide, and the total of the three constituents by the consumption of alkali when the mixture is heated for 15 mins. with excess of the reagent. When warmed in alcoholic solution with zinc carbonate, the free acid and anhydride are precipitated as zinc lactate, the unattacked lactide being then determined in the evaporated and filtered solution by warming with excess of standard alkali, adding a known excess of standard acid and a little potassium ferrocyanide to precipitate the last traces of zinc, and titrating back. The presence of zinc interferes with the end-point of this titration, and the amount of zinc held in solution varies with the amount of lactide present. Lactic acid, lactide, and water form an equilibrium mixture, the position of the equilibrium being the same at 155°, for which $C_{\text{lactide}} \times C^2_{H_2O}/C^2_{\text{acid}} =$ 0·0567. Anhydride is present in such mixtures in amount varying with the previous history of the sample, and not depending on the amount of water present, an effect ascribed to the colloidal nature of the anhydride. F. G. W.

Spontaneous Oxidation of Lactic Esters and Alanine in Presence and in Absence of Catalysts. L. J. SIMON and L. PIAUX (*Bull. Soc. Chim. biol.*, 1924, **6**, 412—423).—Lactic esters are oxidised spontaneously in contact with air or oxygen with the formation of acetaldehyde, ethyl pyruvate, and carbon dioxide. The oxidation is accelerated by warming and agitation, but it is not influenced by light. Alanine, on the other hand, is not spontaneously oxidised except in the presence of sodium hydroxide and finely-divided metallic copper, when it gives rise to pyruvic acid and acetaldehyde. If pyruvates in alkaline solution are agitated in presence of oxygen, a decrease in the quantity of pyruvic acid is observed. The production of pyruvic acid does not necessarily precede the formation of acetaldehyde, which may be derived from α-hydroxyacrylic acid. D. R. N.

Synthesis of Oxalic Acid. C. MATIGNON and C. FAURHOLT (*Compt. rend.*, 1924, **179**, 271—274).—The synthesis of potassium oxalate by the action of carbon monoxide under pressure on potassium carbonate is described. The reverse action, viz., the decomposition of the oxalate in a vacuum, is observed at 370°, is distinct at 420°, and reaches a practicable velocity at 430—440°; for the synthesis it is therefore necessary to employ at least this temperature and a pressure of carbon monoxide greater than that calculated either by the Q/T relation or the Nernst formula from the equation $CO+K_2CO_3=K_2C_2O_4+19{\cdot}8$ cals. At the necessary temperature in the absence of catalysts, the decomposition of the carbon monoxide into carbon dioxide is negligibly small, so that at 470° and with a pressure of 243 atm. of carbon monoxide, potassium carbonate to which is added 2·5% of animal charcoal as a catalyst, is converted in 2½ hours into a product containing 29% (optimum) of potassium oxalate. Under the same conditions, but in the absence of animal charcoal, the yield is only 9·7%. No oxalate is produced under similar conditions using sodium carbonate, since the thermal effect necessitates the use of a much higher pressure. J. W. B.

Complex Compounds of Chromium and Cobalt with Aliphatic and Aromatic Amines. IV. Stereochemistry of Saturated Tervalent Nitrogen. J. MEISENHEIMER (*Annalen*, 1924, **438**, 217—278).—[With L. ANGERMANN and H. HOLSTEN.]—*Pyridochromidioxalates.* trans-*Pyridinium diaquochromidioxalate*, $[Cr(C_2O_4)_2(H_2O)_2]H,C_5H_5N$, (I), fine, lilac crystals, is obtained by double decomposition of the sodium salt with pyridinium nitrate, the *cis* salt being present in the mother-liquors. The *cis* salts of this series are transformed into the *trans* salts in dilute hydrochloric acid solution, the reverse change being brought about by dilute alkalis. Compound (I) is converted into trans-*pyridinium monoaquomonopyridochromidioxalate*, $[Cr(C_2O_4)_2(H_2O)Py]H,C_5H_5N$, reddish-violet crystals, by the action of cold aqueous pyridine, the *cis isomeride* being obtained if excess of pyridine, with only a trace of water, is used. The *dipyridochromidioxalates*, $[Cr(C_2O_4)_2(C_5H_5N)_2]$, are obtained from the diaquo salts when the latter are boiled with pyridine, *cis-trans* isomerism not being observed in this series, the following members of which are described: *potassium*, pale rose needles ($+3H_2O$) or octahedra ($+2H_2O$); *pyridinium* ($+2\frac{1}{2}H_2O$);

sodium (+$1H_2O$); *barium* and *calcium* (+$6H_2O$); *cinchonine*, and *strychnine* salts. *Sodium tripyridochromidioxalate*,

$$[Cr(C_2O_4)_2(C_5H_5N)_3]Na,$$

bluish-red, cubic crystals (anhydrous) or prisms (+$3\frac{1}{2}H_2O$), is obtained by boiling the dried diaquo salts with anhydrous pyridine. The complex *aniline* and *cinchonine* salts are described.

Dimethylethylenediaminechromidioxalates. Ethylene di-p-*toluenesulphonamide*, prisms, m. p. 162—163°, was treated with methyl sulphate and sodium hydroxide to form *ethylene di*-p-*toluenesulphonmethylamide*, needles, m. p. 167—168°, the latter yielding dimethylethylenediamine on hydrolysis with 70% sulphuric acid. *Potassium dimethylethylenediaminechromidioxalate* was isolated in the form of a double salt with potassium iodide, $[Cr(C_2O_4)_2C_4H_{12}N_2]K,KI,2H_2O$, small, dark red crystals, by the action of the base on an aqueous solution of *cis* potassium diaquochromidioxalate at 70°, potassium iodide being added when reaction was complete. The *potassium nitrate double* salt, $[Cr(C_2O_4)_2C_4H_{12}N_2]K,KNO_3,2H_2O$, dark red plates or prisms, the *silver* salt, $[Cr(C_2O_4)_2C_4H_{12}N_2]Ag,H_2O$, bluish-red plates, and the *strychnine* salt, bluish-red needles, are described.

[With E. KIDERLEN.]—*Chloroaminediethylenediamine cobalti* salts. *Praseo*-dichloroethylenediaminecobalti salts react in cold aqueous solution with primary aliphatic and aromatic amines, one of the inner halogen atoms being replaced by the amine. The *violeo* salts yield identical products, but the reaction is much slower. *Chloroanilinediethylenediamine cobaltichloride*, $[Co\ en_2,Ph{\cdot}NH_2,Cl]Cl_2,H_2O$, reddish-violet, hexagonal prisms; *bromide* (+$\frac{1}{2}H_2O$), similar; *iodide, chloride-dithionate*, violet-pink prisms; *nitrate*, dark red crystals; *chloride-nitrate*, violet-pink needles; and d-π-*bromocamphorsulphonate* are described. The *p*-toluidine derivatives of this series decompose more readily than those of aniline. *Chloro*-p-*toluidine diethylenediaminecobaltichloride* (+H_2O), *bromide* (+H_2O), *iodide, dithionate, chloride-nitrate*, and d-π-*bromocamphorsulphonate* are described. The tendency of primary amines to enter the complex ion increases with increasing basicity, aliphatic amines reacting more rapidly than aromatic. *Chloroallylamine diethylenediamine cobaltichloride*, $[Co\ en_2(C_3H_7N)Cl]Cl_2,H_2O$, *bromide, iodide, dithionate*, and d-π-*bromocamphorsulphonate* (+$2H_2O$), are described. The latter could not be resolved by fractional crystallisation. *Chlorobenzylaminediethylenediamine cobaltichloride*,

$$[Co\ en_2(C_7H_9N)Cl]Cl_2{\cdot}H_2O,$$

violet-red needles (anhydrous, lustrous pink plates), *bromide* (+$\frac{1}{2}H_2O$), *iodide, chloride-dithionate, nitrate*, and d-π-*bromocamphorsulphonate*, m. p. 183—185° (decomp.), are described. The latter was separated into the inactive (*trans*) form and *d*- and *l*-(*cis*) forms. *Chloro-ethylaminediethylenediamine cobaltichloride*,

$$[Co\ en_2(C_2H_7N)Cl]Cl_2,H_2O,$$

and *iodide* (anhydrous) were also prepared. The action of benzylamine and ethylamine on the *violeo* salts yields hydroxo-aquo salts. Diethylamine and methylbenzylamine react with *praseo-chloride* with formation of trans*chlorohydroxodiethylenediamine cobaltichloride*, $[Co\ en_2(OH)Cl]Cl,H_2O$, dove-grey crystals (anhydrous, paler and greenish). This yields, on solution in hydrochloric acid, trans*chloroaquodiethylenediamine cobaltichloride*, $[Co\,en_2(H_2O)Cl]Cl_2,H_2O$, dirty, greyish-green needles; on warming with aqueous potassium bromide, *hydroxoaquodiethylenediamine cobaltibromide*, $[Co\,en_2(OH)(H_2O)]Br_2$; and on precipitation from warm aqueous solution with alcohol, *diaquodiethylenediamine cobaltichloride*, $[Co\,en_2(H_2O)_2]Cl_3,2H_2O$, short, red, hexagonal prisms. Dimethylethylenediamine converts the *praseo*-chloride into triethylenediamine cobaltichloride, whilst methylaniline converts it into the *violeo*-chloride and the *complex salt*,

$$[Co_2\,en_5Cl_2]Cl_4,H_2O.$$

[With L. ANGERMANN and H. HOLSTEN.]—*Glycine and sarcosine diethylenediamine cobalti salts. Glycinediethylenediamine cobaltichloride*, $[Co\,en_2(C_2H_4O_2N)]Cl_2,H_2O$, yellowish-red prisms, is obtained by the action of glycine on *praseo*-chloride in presence of sodium carbonate. The d-*π-bromocamphorsulphonate*, thick red prisms, yields the l-*complex* d-*bromocamphorsulphonate* on repeated crystallisation from alcohol and water. The l-*iodide* and l-*dithionate* are described. *Sarcosinediethylenediamine cobaltichloride*,

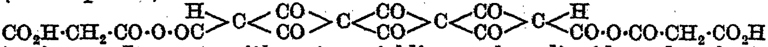
$$[Co\,en_2(C_3H_6O_2N)]Cl_2,1\tfrac{1}{2}H_2O,$$

strawberry-red plates, is obtained similarly, using sodium hydroxide in place of the carbonate. The *iodide* ($+1H_2O$) and *dithionate* ($+1H_2O$) were also prepared. The d-*bromocamphorsulphonate* forms pale red needles or garnet-red prisms containing alcohol and water of crystallisation, or pink needles of the heptahydrate. The latter can be obtained in two forms of $[M]_D$ −923° and +2020°, respectively, the optical activity of the complex ion being due to the cobalt atom alone, the asymmetric nitrogen atom of the sarcosine being inactive. When the mother-liquors from the above salts were concentrated, a *tetrahydrate* separated as a pale red powder, the freshly prepared solution of which had $[M]_D$ +2290°, the value rapidly falling to +2020°, the increased activity being due to the nitrogen atom. The remaining isomerides were only obtained in an impure condition. The d- and l-*iodides* ($+1\tfrac{1}{2}H_2O$), red prisms, $[M]_D$ +1485° and −1530°, and *dithionates* ($+1H_2O$), $[M]_D$ +1530° and −1555°, are described. The action of phenylglycine, *o*-carboxyphenylglycine, and anthranilic acid on the *praseo*-chloride did not proceed analogously to that of the above bases. F. G. W.

Ethyl-*n*-hexylbarbituric Acid and other Derivatives of *n*-Hexylmalonic Acid. A. W. DOX (*J. Amer. Chem. Soc.*, 1924, **46**, 1707—1711).—*n*-Hexyl bromide condenses with ethyl malonate in the presence of sodium ethoxide, giving *ethyl* n-*hexylmalonate*, b. p. 268—270°/749 mm., from which n-*hexylmalonic acid*, m. p. 105—106° (*amide*, m. p. 208°, *anilide*, m. p. 156°), is obtained by hydrolysis with potassium hydroxide. On heating with carbamide and sodium ethoxide at 104°, ethyl hexylmalonate yields n-*hexylbarbituric acid*, m. p. 216°. Methylcarbamide similarly yields 1-*methyl*-5-n-*hexylbarbituric acid*, m. p. 68°. 1-*Phenyl*-5-n-*hexylbarbituric acid*, m. p. 141°, and 1-o-*tolyl*-n-*hexylbarbituric acid*, m. p. 118°, were similarly prepared. *Ethyl ethyl*-n-*hexylmalonate*,

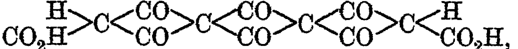
b. p. 280—282°/755 mm., from ethyl ethylmalonate and hexyl bromide, yields *ethyl*-n-*hexylmalonic acid*, m. p. 75°, decomp. at 140°. The ester is converted by carbamide and sodium ethoxide into *ethyl*-n-*hexylbarbituric acid*, small, white crystals, in 96% of the theoretical yield. Ethyl-*n*-hexylbarbituric acid is a somewhat more effective hypnotic than "luminal," being more rapid in its action and less toxic, although the effect is of shorter duration. 1-Methyl-5-hexylbarbituric acid is inert and 1-phenyl-5-hexylbarbituric acid is toxic without hypnotic action. R. B.

Carbon Suboxide. O. Diels, R. Beckmann, and G. Tönnies (*Annalen*, 1924, **439**, 76—96).—Carbon suboxide was prepared by a modification of the method of Ott and Schmidt (cf. A., 1922, ii, 641) which increased the yield from 40 to 55—60%. The hypothesis of Ott and Schmidt that the lack of stability of carbon suboxide, prepared by means of phosphoric oxide, is due to the presence of phosphorus compounds is shown to be incorrect, since specimens prepared from diacetyltartaric anhydride were found to polymerise as rapidly as those obtained by the older method, the stability of Ott and Schmidt's specimens more probably being due to the careful removal of other substances, *e.g.*, acetic acid. By the action of carbon suboxide on acetic acid, a product is obtained which, by loss of acetic anhydride, yields not malonic anhydride as previously suggested (cf. A., 1908, i, 929), but a *mixed anhydride* of acetic and malonic acids, $CO_2H\cdot CH_2\cdot CO\cdot OAc$. With oxalic acid in acetone solution, carbon suboxide yields the β-lactone of β-hydroxy*iso*propylmalonic acid (cf. Meldrum, T., 1908, **93**, 601), carbon dioxide and carbon monoxide also being evolved. Malonic acid in ether or ethyl acetate solutions reacts with 3 mols. of carbon suboxide, probably first to yield a mixed anhydride of keten character, which then reacts with the remaining 2 mols. of the suboxide to yield an exceedingly hygroscopic, yellow *substance* (decomp. 60°) to which the formula



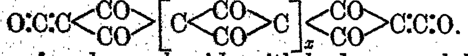
$$\mathrm{CO_2H\cdot CH_2\cdot CO\cdot O\cdot}\begin{matrix}\mathrm{H}\\ \mathrm{OC}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{H}\\ \mathrm{CO\cdot O\cdot CO\cdot CH_2\cdot CO_2H}\end{matrix}$$

is given. It reacts with water, yielding carbon dioxide and malonic acid and with alcohols it yields esters of the acid



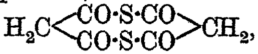
$$\begin{matrix}\mathrm{H}\\ \mathrm{CO_2H}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{H}\\ \mathrm{CO_2H},\end{matrix}$$

together with the corresponding dialkyl esters of malonic acid and acetonedicarboxylic acid (the latter by profound alcoholysis); the *methyl*, m. p. 183·5° (decomp.); *ethyl*, m. p. 150—151° (decomp.); *propyl*, m. p. 132—133°, esters are described. Molecular-weight determinations agree with the suggested formula, and hence the constitution of the corresponding red polymeride of carbon suboxide is probably best represented by the formula,



$$\mathrm{O{:}C{:}C}\!<\!\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\!>\!\left[\mathrm{C}\!<\!\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\!>\!\mathrm{C}\right]_x\!<\!\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}\!>\!\mathrm{C{:}C{:}O}.$$

The reaction of carbon suboxide with hydrogen sulphide depends largely on the proportions of the reactants employed. With excess of hydrogen sulphide, thioacetic acid and carbonyl sulphide are formed, dithiomalonic acid probably being an intermediate product.

In equimolecular proportion, the reaction yields *bi(?)molecular malonic thioanhydride*,  $H_2C<\begin{matrix}CO\cdot S\cdot CO\\CO\cdot S\cdot CO\end{matrix}>CH_2$, m. p. 120—125°, its very slight solubility in all solvents precluding the determination of its molecular weight. With ammonia, it yields the *ammonium* salt of *thiomalonamic acid*, but with aniline yields only malonanilide, hydrogen sulphide being evolved. Heating in a high vacuum at 200° yields carbonyl sulphide and thioacetic acid. Thermal decomposition in the presence of phosphoric oxide yields carbon suboxide, hydrogen sulphide, carbonyl sulphide, carbon subsulphide, and the *unimolecular malonic thioanhydride*, $CH_2<\begin{matrix}CO\\CO\end{matrix}>S$, dark golden, very unstable crystals, m. p. 60°. It has a distinct acid character and reacts with dimethylaniline in dry benzene with evolution of heat, and is therefore probably *ketenthiocarbonic acid*, $CO:CH\cdot CO\cdot SH$. With water, much heat is evolved and malonic acid is formed with evolution of hydrogen sulphide, but if the mixture be kept cool in ice no hydrogen sulphide is formed and *monothiomalonic acid*, a crystalline compound, is produced. This on heating with water yields malonic acid and hydrogen sulphide.

J. W. B.

Configuration of αα′-Dibromodibasic Acids. II. Derivatives of Adipic Acid. A. W. Bernton, H. R. Ing, and W. H. Perkin, jun. (*J. Chem. Soc.*, 1924, **125**, 1492—1502).—Isomeric ethyl and methyl αα′-dibromoadipates have been prepared and condensed with ethyl sodiomalonate and similar compounds to form *cyclo*pentanes. Further evidence is adduced in support of the contention (cf. T., 1921, **119**, 1393) that the αα′-dibromoadipic acid of m. p. 193° is the *dl*- or racemic modification and that of m. p. 139° the *meso*-isomeride. The liquid isomeride of ethyl αα′-dibromoadipate on condensation with ethyl sodiomalonate yielded ethyl *cyclo*pentane-1 : 2 : 2 : 3-tetracarboxylate, which on hydrolysis gave a solid, m. p. 184°, identical with the *cyclo*pentane-1 : 2 : 3-tricarboxylic acid obtained by Perkin and Robinson (*loc. cit.*) from the solid isomeride. The tribasic acid when treated successively with thionyl chloride and concentrated ammonia gave the *triamide*, m. p. 274°. The solid and liquid isomerides of methyl dibromoadipate on condensation with ethyl sodiomalonate formed (in each case) *methyl* cyclo*pentane*-1 : 2 : 2 : 3-*tetracarboxylate*, m. p. 82—84°. Hydrolysis with methyl-alcoholic potassium hydroxide gave *trans*- (m. p. 184°), and with boiling hydrochloric acid a mixture (m. p. *ca.* 154°) of *cis*- and *trans*-*cyclo*pentanetricarboxylic acids. *Ethyl* 2-*acetyl*cyclo*pentane*-1 : 2 : 3-*tricarboxylate*, b. p. 181—190°/16 mm., was obtained on condensing the solid isomeride of ethyl dibromoadipate with ethyl sodioacetoacetate; on hydrolysis, it yielded *trans*-*cyclo*pentane-1 : 2 : 3-tricarboxylic acid. Ethyl sodiobenzoylacetate and the solid isomeride yielded *ethyl* 2-*benzoyl* cyclo*pentane*-1 : 2 : 3-*tricarboxylate*, an oil, b. p. 235—242°/14 mm.; hydrolysis with cold methyl-alcoholic potassium hydroxide gave the trans-cyclo*pentane*-1 : 2 : 3-*tricarboxylate* (the benzoyl group having been eliminated); the liquid isomeride gave the same products. Both isomerides of methyl αα′-dibromoadipate react with methyl sodiocyanoacetate to form *methyl 2-cyano*cyclo*pentane*-1 : 2 : 3-*tricarboxylate*, rhombic prisms, m. p. 83—84°, b. p. 192—196°/12 mm. Cold concentrated hydrochloric acid converts this into the *dimethyl* cyclo*pentanetetracarboxylate*, m. p. 115°. With boiling acid, a mixture of the *cis* and *trans* forms of the *cyclo*pentane-1 : 2 : 3-tricarboxylic acid was obtained. The *liquid isomeride* of *methyl αα′-dibromoadipate* (cf. Stephen and Weizmann, T., 1913, **103**, 271), b. p. 169—170°/14 mm., is converted to the extent of about 50% into the higher melting isomeride during distillation; the change takes place very gradually at the ordinary temperature. The liquid isomeride of ethyl dibromoadipate behaves similarly, but the conversion is more rapid. Sodium ethoxide or methoxide readily brings about the transformation. Two isomeric *methyl αα′-di-iodoadipates*, m. p. 63° and 112°, respectively, were prepared by boiling the dibromo compounds with sodium iodide in methyl-alcoholic solution. The former was almost immediately changed to the latter variety when its solution in methyl alcohol was shaken with 2 mols. of sodium methoxide. Potassium hydroxide in alcohol acts equally well, but the change was much more gradual in the presence of alcoholic ammonia. The di-iodo ethyl esters interacted much less readily with ethyl sodiomalonate than the corresponding dibromo esters. Prolonged boiling of the low-melting isomeride of methyl di-iodoadipate with methyl sodiocyanoacetate gave a small yield of methyl 2-cyano*cyclo*pentane-1 : 2 : 3-tricarboxylate, and the methyl di-iodoadipate which was recovered had been transformed into a variety of high m. p. The *diamide* of *αα′-di-iodoadipic acid*, m. p. 238° (decomp.), was obtained by the action of concentrated methyl-alcoholic ammonia on methyl di-iodoadipate. Both isomerides of methyl dibromoadipate gave the *diamide* of *αα′-dibromoadipic acid*, m. p. 196°. A. C.

Compounds of Malic Acid and Copper. E. Darmois (*Compt. rend.*, 1924, **178**, 1981—1983).—Addition of copper hydroxide to solutions of malic acid resulted in formation of two well-defined salts, $Cu(C_4H_4O_5)_2,2H_2O$, sky-blue crystals, and

$$3CuO,2C_4H_6O_5,4H_2O,$$

green crystals. In the attempt to obtain other salts, some physical properties of the solutions obtained by adding various proportions of copper hydroxide to malic acid were studied, and details of the values obtained are given. H. J. E.

Rotatory Dispersive Power of Organic Compounds. XI. Molecular Weight of Ethyl Tartrate and the Origin of Anomalous Rotatory Dispersion in Tartaric Acid and its Derivatives. T. M. Lowry and J. O. Cutter (*J. Chem. Soc.*, 1924, **125**, 1465—1470).—Measurements of molecular weight and optical rotation of ethyl tartrate in various solvents did not show any parallelism between the rotation and the degree of association of the solute. The authors therefore criticise the suggestion of

Astbury (A., 1923, i, 178) that the dextrorotatory component of tartaric acid is a single molecule, whilst the lævorotatory component is a polymeride in which the structure of the crystal is in part maintained. Anomalous rotatory dispersion is ascribed to intramolecular changes. S. B.

Optical Superposition. V. *d-sec.*-Octyl *i*-Tartrate. T. S. PATTERSON and C. BUCHANAN (*J. Chem. Soc.*, 1924, **125**, 1475—1476).—d-sec.-*Octyl* i-*tartrate* has b. p. 208°/about 4 mm., m. p. 33°, $[\alpha]_D^{17}$ +0·42°. This value of the specific rotation is in contradiction to the principle of optical superposition. S. B.

Dithioformic Acid. T. G. LEVI (*Gazzetta*, 1924, **54**, 395—397).—From potassium dithioformate solution, prepared by the action of potassium sulphide on chloroform (cf. Cambi, *R. Ist. Lomb. Sci. Lett.*, 1910, **43**, II), the corresponding *silver*, $H\cdot CS_2Ag$, and *lead* salts may be obtained as comparatively stable, orange-yellow precipitates; the former begins to darken at 95—100° and the latter at 130—135°. The *zinc* salt is yellowish-white and the *cobalt* salt, deep reddish-brown. The *disulphide*, $(H\cdot CS_2\cdot CS_2\cdot H)_x$, obtained on cautious addition of alcoholic iodine solution to potassium dithioformate dissolved in alcohol, forms a reddish-yellow precipitate, decomp. above 200°. T. H. P.

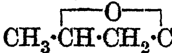
Preparation of Thioacetic Acid. H. T. CLARKE and W. W. HARTMAN (*J. Amer. Chem. Soc.*, 1924, **46**, 1731—1733).—Acetic anhydride or acetyl chloride alone does not react with hydrogen sulphide, but on passing the gas into acetic anhydride containing about 2% of acetyl chloride absorption takes place to the extent of 80% of the quantity calculated on the equation: $(CH_3CO)_2O+H_2S=Me\cdot CO\cdot SH+Me\cdot CO_2H$, and a 70% yield of thioacetic acid, b. p. 88—91·5°, is obtained. Hydrogen chloride and concentrated sulphuric acid also catalyse the reaction, the latter acid also tending to oxidise the hydrogen sulphide, but acetyl bromide is a more effective catalyst than acetyl chloride (cf. Orton, Watson, and Bayliss, T., 1923, **123**, 3081). The reaction proceeds in two stages, the first of which (20—30% absorption) requires only one-tenth of the amount of catalyst required for completion of the reaction. R. B.

Sulphide Acids. II. *iso*Butyl Ether of Thioglycollic Acid [*iso*Butylthiolacetic Acid]. Y. UYEDA and J. KAMON (*J. Chem. Soc. Japan*, 1923, **44**, 1061—1070).—iso*Butylthiolacetic acid*, $CHMe_2\cdot CH_2\cdot S\cdot CH_2\cdot CO_2H$, a pale yellow liquid, b. p. 244°, d^{25} 1·0685, n^{25} 1·4750, is obtained by boiling a solution of the sodium salt of *iso*butyl mercaptan with sodium chloroacetate. The *strontium* (+1·5H_2O), *nickel* (+2H_2O), *cobalt* (+2H_2O), *cadmium* (+H_2O), *copper* (+2H_2O), and *silver* salts are described. It gives a chloride, b. p. 104—105°/13—15 mm., d^{25} 1·1034, n^{25} 1·4780; an *amide*, m. p. 49°; an *ethyl* ester, b. p. 209°, d^{25} 0·9848, n^{25} 1·4550; a *propyl* ester, b. p. 228°, d^{25} 0·9648, n^{25} 1·4550; an iso*butyl* ester,

b. p. 234°, d^{25} 0·9526, n^{25} 1·4530; and a *butyl* ester, b. p. 245°, d^{25} 0·9577, n^{25} 1·4515. K. K.

Catalytic Action. VII. Catalytic Action of Reduced Copper on Acetaldehyde. S. Komatsu and M. Kurata (*Mem. Coll. Sci. Kyoto*, 1924, **7**, 293—295).—Acetaldehyde, when passed over reduced copper heated at 300°, is partly converted into crotonaldehyde, paraldehyde, and metaldehyde. F. G. M.

Polymerisation of Aldols. M. Bergmann and E. Kann (*Annalen*, 1924, **438**, 278—293).—*Acetylcyclo**aldol*** (*paraldol diacetate*),



$CH_3·\overset{\ulcorner\!-O-\!\urcorner}{CH·CH_2·CH}·OAc$, b. p. 156—158°/12 mm., n_D^{20} 1·4425, d_4^{20} 1·100, is obtained by the action of cold acetic anhydride on acetaldol in presence of pyridine. It remains associated to the bimolecular form in benzene, phenol, or glacial acetic acid, but the vapour dissociates gradually at 140° and rapidly at 180°. It does not react with methyl orthoformate, but yields a colourless, viscous *oxime*, b. p. 120—122°/12 mm., n_D^{20} 1·4500. Aldoldimethylacetal affords, similarly, *acetylaldoldimethylacetal*,

$$CHMe(OAc)·CH_2·CH(OMe)_2,$$

b. p. 84—86°/13 mm., which is hydrolysed by cold *N*/1-sulphuric acid to *γ-acetoxy*-n-*butaldehyde*, sour-smelling, mobile liquid, b. p. 72—76°/12 mm. The latter reacts with methyl orthoformate, yielding the dimethylacetal again, and forms the same oxime as the above acetyl*cyclo*aldol. The dimethylacetal is also obtained by the action of methyl orthoformate on paraldol. *Hydracetylacetone monoacetate*, b. p. 84°/12 mm. (*phenylhydrazone*, hexagonal plates, m. p. 115°); *acetopropyl acetate*, $CH_3·CO·CH_2·CH_2·CH_2·OAc$, b. p. 91°/12 mm., n_D^{14} 2·4295, d_4^{14} 1·0186; and *acetobutyl acetate*, b. p. 114—116°/12 mm., $n_D^{13·5}$ 1·4336, $d_4^{13·5}$ 1·002, none of which is associated in solution, are described. γ-Methylglucoside, tetramethyl-γ-methylglucoside, *tetra-acetyl-γ-methylglucoside*, a pale yellow syrup, b. p. 156°/0·3 mm., and tetra-acetyl-β-methylglucoside are unimolecular in solution. The tendency to polymerisation of the aldol *cyclo*acetates is ascribed to the unsaturated affinity of the bridge-oxygen, and is greater the nearer the two carbon atoms thereby connected. F. G. W.

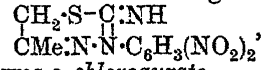
Action of Calcium Hydride on certain Organic Compounds. I. Acetone. C. Porlezza and U. Gatti (*Gazzetta*, 1924, **54**, 491—509).—The condensation of acetone in presence of calcium hydride yields α- and β-*iso*xylitones (cf. Knoevenagel and Blach, A., 1906, i, 964; Knoevenagel and Beer, *ibid.*) and other apparently analogous compounds. In presence of calcium or its oxide, acetone undergoes a condensation which is similar, at least qualitatively, to that effected by the hydride, but the latter acts more energetically in this respect. Under no conditions was it found possible to obtain the compound, b. p. 226—236°, described by Reich and Serpek (A., 1920, i, 249). T. H. P.

Reactions of Chloroacetone 2 : 4-Dinitrophenylhydrazone. C. Bülow and F. Seidel (*Annalen*, 1924, **439**, 48—58).—The condensation of chloroacetone with 2 : 4-dinitrophenylhydrazine at first gives *chloroacetone* 2 : 4-*dinitrophenylhydrazone*,

$$(NO_2)_2C_6H_3{\cdot}NH{\cdot}N{:}CMe{\cdot}CH_2Cl,$$

yellow needles, m. p. 124—125·5°. Prolonged boiling in alcoholic solution converts it into the corresponding *osazone*,

$$(NO_2)_2C_6H_3{\cdot}NH{\cdot}N{:}CH{\cdot}CMe{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2,$$

m. p. 298°. The chlorine atom of the hydrazone has a greatly increased reactivity and reacts with a large number of amines. One mol. of ammonia condenses with 2 mols. of the phenylhydrazone to yield the *imine*, $NH[CH_2{\cdot}CMe{:}NR]_2$, where R is the hydrazone residue, m. p. 215°, and methylamine yields the corresponding *methylimine*, microscopic yellow needles, m. p. 222°. Camphylamine yields a *camphylimino* derivative, m. p. 184—185°, pyridine a quaternary *pyridinium* salt, $CMe{:}NR{\cdot}CH_2{\cdot}NC_5H_5Cl$, greenish-yellow, becoming red at 180—190°, m. p. 201—203°. Piperidine yields a *tertiary base*, m. p. 200° (decomp.), whilst quinoline yields a *compound* analogous to that obtained with pyridine, but which retains 1 mol. of water of crystallisation very tenaciously and is isolated as the *osazone*, m. p. 295° (much decomp.). The action of phenylhydrazine on chloroacetone 2 : 4-dinitrophenylhydrazone yields the *mixed osazone*, carmine-red needles, m. p. 232°. By the action of sodium acetate in alcoholic solution on chloroacetone 2 : 4-dinitrophenylhydrazone, the corresponding *phenylhydrazone* of *acetonyl acetate* (cf. Henry, A., 1873, 379), long, flat, yellow tablets, m. p. 106—107°, is obtained, whilst by the action of potassium thiocyanate the corresponding *thiocyanoacetone* 2 : 4-*dinitrophenylhydrazone*, golden, iridescent crystals, m. p. 127—128°, is formed. By intramolecular rearrangement this compound forms a cyclic *compound*,  $\begin{array}{l}CH_2{\cdot}S{-}C{:}NH\\ CMe{:}N{\cdot}N{\cdot}C_6H_3(NO_2)_2\end{array}$, which is isolated as its *hydrochloride*. It forms a *chloroaurate*,

$$(C_{10}H_9O_4N_5S)_2,HAuCl_4,HCl.$$

With potassium xanthate in the cold, chloroacetone 2 : 4-dinitrophenylhydrazone forms a *xanthate*, $CMe({:}NR){\cdot}CH_2{\cdot}S{\cdot}CS{\cdot}OEt$, fine needles, m. p. 77—78° (cf. this vol., i, 573). J. W. B.

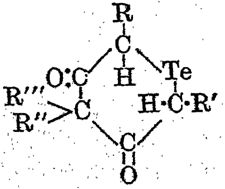
Special Examples of Grignard's Reaction. H. Goudet and H. Paillard.—(See i, 1055.)

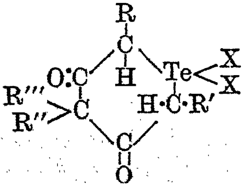
Dehydration of some new Pinacones. R. Locquin and L. Leers (*Compt. rend.*, 1924, **178**, 2095—2098).—Dehydration of a series of pinacones, as in the case of those already studied (Meerwein, A., 1913, i, 485; Locquin and Sung, this vol., i, 613), results in formation only of $CRMe_2{\cdot}CO{\cdot}Me$ from $CRMe(OH){\cdot}CMe_2{\cdot}OH$; the alternative transformation into $CMe_3{\cdot}CO{\cdot}R$ does not appear to occur. This was shown both by oxidation of the resulting ketone to the corresponding acid and by comparison with the latter type of ketone prepared by condensation of pivaloyl chloride with organo-zinc compounds of the type $R{\cdot}Zn{\cdot}I$. The following are described: γγ-*Dimethylhexan*-β-*one*, b. p. 149°/745 mm., d_4^0 0·838, *semicarbazone*, m. p. 119·5°, *oxime*, m. p. 58°, b. p. 100—101°/12 mm.;

αα-dimethylpentoic acid, b. p. 98—99°/9 mm., *chloride*, b. p. 45°/10 mm., *methyl* ester, b. p. 144—145°; *βγ-dimethylheptane-βγ-diol*, *γγ-dimethylheptan-β-one*, b. p. 169·5°/735 mm., d_4^{11} 0·834, *semicarbazone*, m. p. 130—131°; *αα-dimethylhexoyl chloride*, b. p. 56°/10 mm., *amide*, m. p. 92°; *ββ-dimethylheptan-γ-one*, b. p. 164°/735 mm., d_4^{11} 0·823, *semicarbazone*, m. p. 142—143°; *γγ-dimethyloctan-β-one*, b. p. 75°/10 mm., d_4^{0} 0·843, *semicarbazone*, m. p. 106°; *αα-dimethylheptoic* acid, b. p. 130°/12 mm., *chloride*, b. p. 74—75°/10 mm., *amide*, m. p. 101—102°; *ββ-dimethyloctan-γ-one*, b. p. 72°/10 mm., d_4^{0} 0·834, *semicarbazone*, m. p. 139—140°. H. J. E.

cyclo**Telluropentanediones and *cyclo*Telluripentanedione Dihalides.** G. T. MORGAN and H. D. K. DREW (*J. Chem. Soc.*, 1924, **125**, 1601—1607).—The behaviour of a series of tellurium β-diketones towards hydroxylamine shows that these compounds are diketonic in structure, since they yield dioximes as well as monoximes. It is concluded that the cyclic tellurium β-diketones and their corresponding dihalides belong to two new types of cyclic organometalloidal compounds, that represented by (I) being

(I.)





(II.)

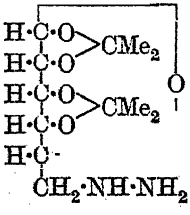
designated cyclo*telluropentane*-3 : 5-*diones* and (II) cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dihalides*; X may be Cl, Br, or I, and R, R′, etc. may stand for hydrogen atoms or similar or dissimilar alkyl or arylalkyl (*e.g.*, benzyl) groups, but not for phenyl or other purely aromatic groups. cyclo*Telluri*-4 : 4-*dimethylpentane*-3 : 5-*dione*-1 : 1-*dichloride*, m. p. 194°, prepared by refluxing a chloroform solution of dimethylacetylacetone with tellurium tetrachloride, was converted by aqueous potassium metabisulphite into cyclo*telluro*-4 : 4-*dimethylpentane*-3 : 5-*dione*, m. p. 124—125°. Oximation of tellurium acetylacetone gave cyclo*telluropentane*-3 : 5-*dionedioxime*, m. p. indefinite; similarly, tellurium ethyl acetylacetone yielded cyclo*telluro*-4-*ethylpentane*-3 : 5-*dionedioxime* (decomp. 192° after darkening at 173°). Steric hindrance manifests itself as substitution proceeds, monoximes being formed when oximation is conducted in presence of dilute acetic acid, and dioximes under more drastic conditions in alkaline solution. cyclo*Telluro*-4 : 4-*dimethylpentane*-3 : 5-*dione*-5-*monoxime* has m. p. 183—184° or 180° when crystallised from benzene or alcohol, respectively; the corresponding *dioxime* decomposes at 235°. cyclo*Telluro*-2 : 4-*dimethylpentane*-3 : 5-*dione*-5-*monoxime* and the corresponding *dioxime* decompose respectively at 168° and 198°.

Derivatives of tellurium *n*-butyrylacetone exhibit isomerism of the Hantzsch–Werner type and two isomeric dioximes have been isolated which are provisionally designated as α- and β-forms, and may have respectively the *syn-* and *anti*-configurations. α-cyclo-*Telluro-2-ethylpentane-3 : 5-dionedioxime*, m. p. 149°, and its β-*isomeride*, m. p. 183°, are produced in the ratio of 5 : 1 by oximation in alkaline solution.

Three dynamic isomerides of β-diketones exist as evidenced by the interaction of acetylacetone and its homologues with metallic compounds and selenium and tellurium tetrachlorides. (1) A *trans*-monoenolic form reacts in the case of the formation of derivatives of Cu, B, Si, Ge, Ti, Sn, and Zr. (2) A *cis*-monoenolic form takes part in condensation with $SeCl_4$. (3) A diketonic form interacts with $TeCl_4$ to form a six-membered ring in which enolisation can only occur under conditions of strain tending to disrupt the ring. C. J. S.

The Anthocyanin Pigment of *Ipomœa hederacea*. Y. Yamaguchi (*Ber. deut. bot. Ges.*, 1924, **42**, 144—147).—The anthocyanin was extracted from the flowers of *Ipomœa hederacea* by treatment with methyl alcohol containing 3% of hydrochloric acid and precipitated with ether. A very small yield of reddish-brown, rhombic crystals was obtained by mixing the crude product with 1% hydrochloric acid and a large volume of 1·5% picric acid solution at 50° and allowing to stand for 2 months. The anthocyanin is tentatively named hederacein. The sugar obtained on acid hydrolysis of the crude product and removal of the anthocyanidin was almost certainly dextrose and not galactose. C. T. G.

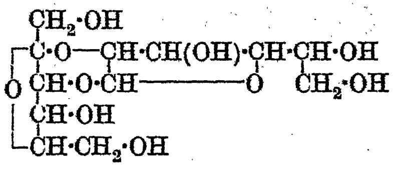
Nitrogenous Derivative of Diacetoneglucose. E. Merck Chemische Fabrik (D.R.-P. 382913; from *Chem. Zentr.*, 1924, i, 1591).—*Hydrazinediacetoneglucose* (annexed formula), from toluene-*p*-sulphonyldextrosediacetone and hydrazine, has m. p. 96—97°, $[\alpha]_D$ +83°. It forms an *iso*propylidene *compound*, and a benzylidene *compound*, m. p. 99—100°, $[\alpha]_D$ +144° in *s*-tetrachloroethane. G. W. R.



Mechanism of the Oxidation of Lævulose in Phosphate Solutions. O. Meyerhof and K. Matsuoka (*Biochem. Z.*, 1924, **150**, 1—11).—The spontaneous oxidation of lævulose in concentrated phosphate solutions, described by Warburg and Yabusoe (this vol., i, 713), is shown to be due to the catalytic action of a metal, since the reaction is inhibited by the presence of potassium cyanide and of sodium pyrophosphate, which would lead to the formation of stable complex salts; it is accelerated by the addition of copper, iron, and manganese, this acceleration being abolished by the simultaneous addition of cyanide, and it takes place equally well in solutions of arsenates. C. R. H.

Action of Heat on Sucrose. A. Pictet and N. Andrianoff (*Helv. Chim. Acta*, 1924, **7**, 703—707; cf. this vol., i, 499).—When sucrose (m. p. 183°) is heated at 185—190°/10—15 mm. until it has lost 5% of its weight, iso*saccharosan*, $C_{12}H_{20}O_{10}$, is obtained, which, when precipitated from methyl-alcoholic solution by addition of acetone, forms a white, hygroscopic, amorphous powder with a bitter taste, m. p. 94—94·5°, $[\alpha]_D^{22}$ +64·0°; it rapidly undergoes hydrolysis to dextrose and lævulose in aqueous solution. The *hexa-acetate* forms colourless prisms, m. p. 79—80°. If the heating be continued until the sucrose has lost 10% of its weight, caramelan, $C_{24}H_{36}O_8$ (cf. Cunningham and Dorée, A., 1917, i, 513), is obtained as a pale yellow, hygroscopic, amorphous substance, much purer than when produced in an open vessel. It has m. p. 144—145°, $[\alpha]_D^{22}$ +80·0°. Further heating of sucrose, until 15% of the weight has been driven off, leaves caramelen, $C_{36}H_{50}O_{25}$, a brown, non-hygroscopic powder, m. p. 204—205°, $[\alpha]_D^{22}$ +65·4°. W. A. S.

Constitution and Synthesis of *iso*Saccharosan. A. Pictet and P. Stricker (*Helv. Chim. Acta*, 1924, **7**, 708—713).—*iso*Saccharosan (cf. preceding abstract) reduces Fehling's solution to half the extent that it should do if the reduction depended on hydrolysis to a mixture of dextrose and lævulose. Moreover, *iso*saccharosan yields an *osazone*, $C_{24}H_{32}O_9N_4$, m. p. 124—125°, in addition to glucosazone, which is the chief product of the reaction. These results indicate that the substance is not a simple anhydride of sucrose, a constitution for which would be difficult to frame. Sucrose is converted at its melting point without loss of weight (cf. Gelis, *Ann. Chim.*, 1859, [iii], **57**, 234) into a mixture of dextrose and lævulosan; in accordance with this it is found that *iso*saccharosan is formed when a mixture of lævulosan and dextrose is heated at 185°/15 mm. until 5% of the total weight is lost. Likewise, if a mixture of glucosan and lævulosan be similarly heated, *iso*saccharosan is formed, no loss of weight taking place in this case. To *iso*saccharosan is attributed the constitution:



Preliminary experiments indicated that by treating *iso*saccharosan with cold 5% ammonia, *iso*sucrose could be obtained. W. A. S.

Glycogen. I. Partial Methylation, and the Isolation of Methylated Glucoses. A. K. Macbeth and J. Mackay (*J. Chem. Soc.*, 1924, **125**, 1513—1521).—Glycogen was alkylated by the repeated action of methyl sulphate in the presence of sodium hydroxide. After three methylations, the product contained 26·7% OMe. Methyl alcohol was then used to keep the product in solution, whereby ultimately a compound with more than 36·4% OMe, corresponding with an introduction of 2—3 methyl groups for each glucose residue, was isolated. Either steric hindrance or physical condition hinders further alkylation. A product containing 36·4% OMe had $[\alpha]_D$ +179·83° in chloroform. Hydrolysis with methyl-alcoholic hydrogen chloride yielded (*a*) almost pure trimethyl methylglucoside, which on treatment with methyl iodide and silver oxide was converted into 2 : 3 : 5 : 6-tetramethyl methylglucoside and therefore contained the butylene oxide linking. Hydrolysis with 6% hydrochloric acid changed it to 2 : 3 : 6-trimethylglucose with constants in good agreement with those of the crystalline 2 : 3 : 6-trimethylglucose from cellobiose, cellulose, and starch; (*b*) a dimethyl methylglucoside belonging to the butylene oxide series which was hydrolysed to a dimethylglucose differing from the 2 : 3-compound described by Irvine and Scott (T., 1913, **103**, 575) and possibly a 2 : 5-derivative, and (*c*) a probable mixture of mono- and di-methyl methylglucosides. It was possible to use glycogen possessing a fairly high nitrogen content in the above methylations; the nitrogen disappeared in the early stages and the products did not differ from those in which rigorously purified material was used. The close agreement between starch and glycogen on methylation and the similarity of the products on hydrolysis, indicates that the polysaccharides are built up from the same basal unit, and that the various formulæ proposed for starch may also be applied to glycogen. A. C.

Redetermination of the Heat of Combustion of Glycogen with Special Reference to its Physiological Importance. W. K. Slater (*Biochem. J.*, 1924, **18**, 621—631).—The heat of combustion of glycogen monohydrate in dilute solution is 3836 cals. per gram. S. S. Z.

Cellulose Nitrate and Camphor. J. B. Nichols.—(See i, 972.)

Soluble Cellulose Esters of Higher Ethylenic Fatty Acids. H. Gault and [Mlle.] M. Urban (*Compt. rend.*, 1924, **179**, 333—334).—In continuation of previous work (cf. Gault and Ehrmann, A., 1923, i, 757), *cellulose triundecylenate*, m. p. (indef.) above 190°, has been prepared by allowing undecylenyl chloride to act, in toluene, on hydrocellulose, previously saturated with a mixture of toluene and excess of pyridine, at 110—120° for 2 hours. The ester is hydrolysed only with great difficulty, and it is therefore not possible to determine the corresponding acid in this manner. J. W. B.

A Substance giving a Blue Colour with Iodine in the Asci of Lichens (*iso*Lichenin). H. Ziegenspeck (*Ber. deut. bot. Ges.*, 1924, **42**, 116—119).—A compound, giving a blue coloration with iodine, to which the name iso*lichenin* is given, has been isolated from an extract of the apothecia of the lichen *Xanthoria parietina* and also from other species. It is a carbohydrate, related to starch, stable towards diastase, and giving dextrose and a little methylpentose on complete hydrolysis with sulphuric acid. It has been detected in the vegetative thallus of only one species—*Cetraria islandica*; in the hymenium of several, and in the young asci of a large number of species. It occurs in the asci until they are almost fully developed, but disappears with the development of the spores, being converted into glycogen. *iso*Lichenin is considered to have the function of a reserve food material. C. T. G.

Hydrocellulose. H. Gault and B. C. Mukerji (*Compt. rend.*, 1924, **179**, 402—405).—The formation of hydrocellulose by the action of dilute sulphuric acid on cellulose has been studied systematically, the increase in the copper number, determined by the method previously described (this vol., ii, 280), giving a measure of the degradation. The rate of formation of hydrocellulose varies directly with the strength of the acid, the time and temperature of immersion, and the temperature of drying. With 5% sulphuric acid, the degradation begins to be appreciable only at 70°. Hauser and Herzfeld's observation (A., 1915, i, 941) that the copper number of hydrocellulose falls to that of pure cellulose on prolonged extraction with boiling water was not confirmed. R. B.

Action of Aqueous Sulphurous Acid on Lignocellulose. C. F. Cross and A. Engelstad (*J. Soc. Chem. Ind.*, 1924, **43**, 253—257T).—The process for the manufacture of cellulose from wood by digestion with a 7% solution of sulphurous acid, free from sulphuric acid (Brit. Pat. 202016, 1922), proves that sulphonation is a direct reaction of sulphurous acid with certain groups of the lignone complex. The secondary effects which differentiate the products of the sulphurous acid process from those of the bisulphite process are the degree of sulphonation, deoxidation of CO groups, and condensation of the sulphonated complex. Analogous reactions are observed with cinnamaldehyde under the same treatment, but not with benzaldehyde or dextrose. Dextrose, however, is partly broken down with formation of acetic acid and caramel, whilst elementary sulphur and sulphur-oxygen by-products are detected. Digestion of oil of turpentine with aqueous sulphurous acid also forms small quantities of sulphur. Digestion of cotton cellulose with pure aqueous sulphurous acid leads to a pronounced degradation of the cellulose, indicating the necessity for synchronising the exposure of the wood cellulose by removal of lignone with the substantial exhaustion of the free sulphurous acid in the digestion liquor. One of the characteristic features of this process is the production of sulphuric acid as the result of deoxidation of certain groups of the lignone, and the conditions have been studied for limiting this phase of the reaction. Chemical attack on the cellulose is considerably promoted by fine subdivision of the raw material without a corresponding intensification of the reaction with the lignone. J. F. B.

Lignosulphonic Acid obtained by the Action of Sulphurous Acid on Spruce Wood. C. Dorée and L. Hall (*J. Soc. Chem. Ind.*, 1924, **43**, 257—263T).—The liquor obtained by digestion of wood with free sulphurous acid differs from that of the ordinary digestion with calcium hydrogen sulphite in its lower degree of sulphonation, its tanning qualities, and its capacity to form gels, these pronounced colloid qualities being associated with the lower temperature of digestion, *viz.*, 100—110°. The lignosulphonic acid has been separated by prolonged dialysis and contains only 5·5% of sulphur as against 7·3% for the bisulphite product. Its empirical formula is $C_{\text{[illegible]}}H_{\text{[illegible]}}O_{12}S$, and according to its reactions with α-naphthylamine it consists practically entirely of a substance of Klason's α (aldehydic) type of lignone. The characterised groups in this complex are summarised in the expression

$$C_{21}H_{15}O_2(SO_3H)(OH)_2(CH_2{\cdot}OH)(CH{\cdot}OH)(CHO)(OMe)_2.$$

On heating with 5% nitric acid, these groups are respectively changed with the following result,

$$C_{22}H_{22}O_5(NO_2)_2(OH)_3(CO)(CO_2H)(CO_2H)(OMe),$$

the nature of the modification of the changed methoxyl group being unexplained. The reactions of this nitro compound on reduction, giving with loss of ammonia a nitrogen-free ketone with three CO groups, show no analogy with the aromatic type and the behaviour of the system generally recalls that of certain unsaturated terpenes of the cholesterol series. Further oxidation by 32% nitric acid gives oxalic acid and a substantial yield of an acid, $C_{20}H_{24}O_{12}(CO_2H)_6(NO_2)_2$. The persistence of the C_{26} complex through all these reactions with a resistant nucleus of the order of C_{20} suggests that the nucleus of lignone is hydroaromatic in character, consisting of a complex of reduced rings somewhat resembling the reduced benzophenanthrene hydrocarbon formulated by Schrauth (A., 1923, i, 443). This involves the general absence of oxygen linkings, the direct attachment of the side groups, including the CHO group, to the carbon atoms of the ring, and the presence of double linkings in the reduced ring. J. F. B.

Preparation of αβγ-Triaminopropane and Formation of Complex Metallic Derivatives. W. J. POPE and F. G. MANN (*Compt. rend.*, 1924, **178**, 2085—2086; cf. Curtis and Hesse, A., 1901, i, 70).—From citric acid the following substances were successively prepared: Acetonedicarboxylic acid, di*iso*nitrosoacetone, diaminoacetone, diacetyldiaminoacetoxime, αβγ-*triaminopropane*. The yield at each stage is stated to be satisfactory. The base is converted into *cobaltiditriaminopropane chloride* and *rhodiditriaminopropane chloride*. H. J. E.

Preparation of a Derivative of Hexamethylenetetramine. R. WOLFFENSTEIN (D.R.-P. 382904; from *Chem. Zentr.*, 1924, i, 968).—*Hexamethylenetetramine formate* is crystalline and has m. p. about 60°. G. W. R.

Synthesis of Hydroxyamines by the Curtius Method. P. A. LEVENE and J. SCHEIDEGGER (*J. Biol. Chem.*, 1924, **60**, 179—181).—Ethyl β-hydroxybutyrate is converted successively into β-*hydroxybutyrihydrazide,* m. p. 119—120°, β-hydroxybutyrazide, and *di*-β-*hydroxypropylacetamide* (*picrate*, m. p. 118—119°). The latter is hydrolysed to β-hydroxypropylamine (*chloroplatinate*, m. p. 210° after softening at 205°). C. T. G.

Formation of Bismuthamines. A. C. VOURNAZOS (*Compt. rend.*, 1924, **178**, 2089—2092).—A brief description of a series of bismuthamines (cf. A., 1923, i, 759) with their formulæ; these substances have been prepared by combination of halides of tervalent bismuth with salts of ammonium, of various types of amines and of alkaloids. Bismuth nitrate and sulphate also yield similar products. The co-ordination number of the bismuthomonoamines is 4, whilst that of the triamines is 6. The compounds resulting from the action of a bismuth halide, BiX_3, on an amine salt, RNH_3Z, are identical with those derived from BiZ_3 and RNH_3X if the affinity of bismuth for X is greater than that for Z. H. J. E.

N-Alkylamino Fatty Acids and their N-Acyl Derivatives. H. Scheibler (D.R.-P. 386743; from *Chem. Zentr.*, 1924, i, 1592—1593; cf. Scheibler and Baumgarten, A., 1922, i, 655).—The following new compounds are mentioned: *ethyl cyanobenzyl-α-aminopropionate*; *benzylidenealanine*; N-*benzylalanine hydrochloride*, m. p. 258°. G. W. R.

Chain-forming Reactions of the Amides of α-Hydroxy-acids. A. Schmuck (*Biochem. Z.*, 1924, **147**, 193—202).—The amides of glycollic and lactic acids, obtained by treating the corresponding cyclic anhydrides with ammonia, yield, when heated in a stream of ammonia at 160—200°, *amidides* or *oxyamidides*, $OH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, hygroscopic crystals, m. p. 86°, and $CHMe(OH){\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO{\cdot}NH_2$, small, hygroscopic tables, m. p. 52°, respectively, which give the biuret and alkaloidal precipitation reactions and are closely related to peptides. The compound thus prepared from lactamide yields on hydrolysis with 5% hydrochloric acid, alanine and lactic acid. In the case of glycollamide, the yield of amidide is small, and an amorphous substance, $C_4H_6O_2N_2$, containing 3·77% of amide nitrogen, is also obtained. J. P.

Relation between Crystal Structure and Constitution of Carbon Compounds. II. Crystallography of further Simple Substitution Products of Methane. I. E. Knaggs (*J. Chem. Soc.*, 1924, **125**, 1441—1444).—A crystallographic description is given of chlorobromoacetomethylamide, chlorobromoacetoethylamide, dichloroacetoethylamide, dichloroacetomethylanilide, and dichloroacetoethylanilide (cf. McKie, this vol., i, 715). S. B.

Action of Hydroxylamine on Ethyl Tartrate. A. J. A. Guillaumin (*Compt. rend.*, 1924, **178**, 1986—1988).—An alcoholic solution of ethyl tartrate ($\frac{1}{2}$ mol.) to which hydroxylamine (2 mols.) has been added, when kept at the ordinary temperature, deposits crystals of *tartramhydroxamic acid*, $CO(NH_2){\cdot}[CH{\cdot}OH]_2{\cdot}C(OH){:}N{\cdot}OH$, m. p. 170—172° (decomp.), $[\alpha]_D^{18}$ 96° 30′, *tetra-acetyl* derivative, m. p. 105°, *tribenzoyl* derivative, m. p. 203°. The substance exhibits mutarotation and, unlike other hydroxamic acids, forms no precipitate with copper acetate; further, ferric chloride gives with it a red coloration on standing. The structure is thus probably of the type $R{\cdot}CO{\cdot}NH{\cdot}OH$, which is rearranged as above on solution in water. H. J. E.

Heat of Formation of Calcium Cyanamide. N. Kameyana (*J. Faculty Eng., Tokyo Imp. Univ.*, 1923, **13**, 61—71).—The author criticises the calculations of the heat of formation of calcium cyanamide given by Thompson and Lombard (*Met. Chem. Eng.*, 1910, 8, 682) and Dolch (A., 1921, ii, 17). E. M. C.

Behaviour of Calcium Cyanamide when Heated in Nitrogen at High Temperatures. N. Kameyana (*J. Faculty Eng., Tokyo Imp. Univ.*, 1923, **13**, 75—102).—On heating calcium cyanamide in nitrogen to temperatures above 1250°, considerable loss occurred with evolution of nitrogen and severe corrosion of the porcelain reaction tube over a considerable distance. It is suggested that the calcium cyanamide sublimed at this temperature and that the vapour reacted with the porcelain. E. M. C.

Preparation of Guanidinium Salts from Calcium Cyanamide. J. S. Blair and J. M. Braham (*Ind. Eng. Chem.*, 1924, **16**, 848—852).—A cold, filtered, aqueous extract of calcium cyanamide is neutralised with sulphuric acid, and evaporated below 80° to a cyanamide content of 165 g. per l. Ammonium nitrate (2 mols. per mol. of cyanamide) is added, and the solution heated slowly to 155°, this temperature being maintained for 3 hours. The hot solution is filtered, the guanidine nitrate crystallising on cooling the filtrate. About 80% of the cyanamide is converted into guanidine. [Cf. *B.*, 1924, 806.] F. G. W.

Peralkylated Guanidines. II. H. Lecher and F. Graf (*Annalen*, 1924, **438**, 154—169; cf. A., 1923, i, 761).—Pentamethylguanidine combines with ethyl iodide in ether solution to form *pentamethylethylguanidinium iodide*, colourless crystals, which unites with iodine to produce the corresponding *tri-iodide*, m. p. 58—59°. NNS-*Trimethyl*-N′-*ethyl*-ψ-*thiocarbamide*, $NMe_2\cdot C(:NEt)\cdot S\cdot Me$, an oil, b. p. 69·2—69·5°/12 mm., is obtained by treating *NN*-dimethyl-*N′*-ethylthiocarbamide (Billeter, A., 1893, i, 575) with methyl sulphate; when it is heated at 100° with dimethylamine in presence of mercuric chloride, NNN′N′-*tetramethyl*-N″-*ethylguanidine*, an oil, b. p. 55·5°/11 mm., is obtained. The latter combines with methyl iodide to give the same pentamethylethylguanidinium iodide as before; addition therefore takes place in both cases at the imino group, and presumably salt-formation takes place in the same way, not, as hitherto supposed, at one of the amino groups.

Guanidinium iodide, prepared by dissolving the carbonate in hydriodic acid, does not form a tri-iodide. *Pentamethylguanidinium* and *hexamethylguanidinium iodides* were obtained in a similar way; the latter yields a *tri-iodide*, red leaflets, m. p. 118—120°. *Hexamethylguanidinium hydroxide* can be obtained only in aqueous solution, best by treating the iodide with thallium sulphate and the resulting sulphate with barium hydroxide. A dilute solution is tolerably stable, but decomposition takes place when it is boiled alone or when sodium hydroxide is present, or even when it is concentrated under diminished pressure, the products of the decomposition being tetramethylcarbamide and dimethylamine.

Guanidinium hydroxide and its alkyl derivatives are bases comparable in strength with the alkali hydroxides. Pentamethylguanidinium hydroxide precipitates from solutions of their salts the hydroxides of the alkaline-earth and heavy metals. W. A. S.

Constitution of Thiocarbamide and "Thiuronium" Salts. H. Lecher and C. Heuck (*Annalen*, 1924, **438**, 169—184).—It is suggested that the salts of carbamide and of thiocarbamide be termed "uronium" and "thiuronium" salts, respectively. When thiocarbamide forms a salt, the hydrogen of the acid attaches itself to the sulphur atom because pentamethylthiuronium iodide (tetramethylthiocarbamide methiodide, Delépine, A., 1911, i, 23) may be obtained by combining with methyl iodide either *NNN'N'*-tetramethylthiocarbamide or *NNN'S*-tetramethyl-ψ-thiocarbamide. In the first case, reaction proceeds rapidly in ethereal solution; in the second, the two reagents were mixed without a solvent, as it was found that in ethereal solution only 10% of the product had separated after two days. The two products were proved to be identical by converting them into the corresponding *picrate*, m. p. 92—93·5°.

NN-Dimethylthiocarbamyl chloride (Billeter, A., 1893, i, 575) interacts with diethylamine in hot benzene to yield NN-*dimethyl-*N'N'*-diethylthiocarbamide*, an oil, b. p. 119—120°/10 mm. Methylthiocarbimide and diethylamine unite in aqueous suspension to form N-*methyl-*N'N'*-diethylthiocarbamide*, $NHMe\cdot CS\cdot NEt_2$, m. p. 36—37·5°; when the latter is treated in hot methyl alcohol with methyl sulphate, NS-*dimethyl*-N'N'-*diethyl*-ψ-*thiocarbamide*, $NMe{:}C(SMe)\cdot NEt_2$, an oil, b. p. 79—80°/10—11 mm., is obtained. When *NN*-dimethyl-*N'N'*-diethylthiocarbamide or *NS*-dimethyl-*N'N'*-diethyl-ψ-thiocarbamide is treated with methyl iodide, or when *NNS*-trimethyl-*N'*-ethyl-ψ-thiocarbamide is treated with ethyl iodide, NNS-*trimethyl*-N'N'-*diethylthiuronium iodide*, $SMe\cdot C(NEt_2){:}NMe_2I$, m. p. 94—95°, is obtained. The three products were conclusively proved to be identical by preparing from each the corresponding *picrate*, m. p. 80—83°. These results need further investigation. Pentamethylthiuronium hydroxide solutions, obtained by treating the iodide with sodium hydroxide, decompose even at room temperature, tetramethylcarbamide and methyl mercaptan being formed. The base was found to be comparable in strength with the alkali hydroxides. W. A. S.

Chemical Behaviour of α- and β-Hydroformamine Cyanides (Methyleneaminoacetonitriles). H. W. Rinehart and T. B. Johnson (*J. Amer. Chem. Soc.*, 1924, **46**, 1653—1661; cf. this vol., i, 625).—Although α-hydroformamine cyanide, m. p. 129°, yields the hydrochloride of ethyl aminoacetate on hydrolysis with alcoholic hydrogen chloride (Jay and Curtius, A., 1894, i, 162; 1899, i, 9; Klages, A., 1902, i, 354), the β-compound, m. p. 86°, merely decomposes to ammonium chloride and a nitrogen derivative of unknown constitution. When hydrolysed in alkaline solution the α-isomeride yields ammonia equivalent to one-half of its nitrogen, whilst the β-compound readily gives off two-thirds of its nitrogen as ammonia. Hydrolysis is less ready with sulphuric acid and the amount of ammonia produced is less, but, in the case of the β-isomeride, increases with the concentration of the acid. Both isomerides are slowly hydrolysed in boiling aqueous solution, the α-compound giving off ammonia rapidly at first, but the rate of production rapidly falls off, whilst the β-compound gives off ammonia slowly at a nearly constant rate up to 17% of its nitrogen, as compared with 40% for the α-isomeride. α-Hydroformamine cyanide yields with hydrogen sulphide and alcoholic ammonia a white, crystalline *substance*, $C_8H_{12}N_5 \cdot CS \cdot NH_2$, m. p. 152—153° on rapid heating, 125—140° (decomp.) in the ordinary way, prolonged treatment giving dithiopiperazine or a thiopolypeptide. β-Hydroformamine cyanide similarly yields a colourless, crystalline *substance*, $C_7H_{12}N_4(CS \cdot NH_2)_2$, m. p. 148° (decomp.). An examination of the absorption spectra of the two isomerides in acetone solution supports the view that neither substance contains free ethylenic linkings. R. B.

Butenonitriles. IV. P. Bruylants (*Bull. Soc. chim. Belg.*, 1924, **33**, 331—338).—During the preparation of vinylacetonitrile by the interaction of allyl bromide and cuprous cyanide (A., 1922, i, 817, 924), diallyl is sometimes produced, but the cause is unknown. Vinylacetonitrile is converted into an equilibrium mixture of crotono- and *iso*crotono-nitriles by sodium phenoxide in the presence of phenol, and by aliphatic mono- and di-amines, but not by acidic reagents. Aqueous *N*/10-sodium hydroxide solution also converts vinylacetonitrile into a mixture of the two crotononitriles and some crotonamide, whereas *N*/2 ethyl-alcoholic sodium hydroxide transforms it almost quantitatively into β-ethoxybutyronitrile, whilst an *N*/4-sodium hydroxide solution in alcohol–water (3 : 1 by vol.) gives a mixture of the two isomeric crotononitriles and β-ethoxybutyronitrile. Vinylacetonitrile, when treated with 1 mol. of sulphuric acid, gives a 50% yield of vinylacetic acid, b. p. 72·6—72·8°/13 mm., 169—169·2°/764·3 mm., m. p. —38·2°, d_4^{20} 1·0091, n_D^{20} 1·4252, together with traces of crotonic acid and amide; the vinylacetic acid is identified by conversion into βγ-dibromobutyric acid, and by the close similarity of its absorption spectrum curve with that of vinylacetonitrile. Vinylacetic acid when heated under reflux for 24 hours is converted into crotonic acid, which probably contains some *iso*crotonic acid. Sodium vinylacetate is stable in aqueous solution, but in sodium hydroxide solution is partly converted into sodium crotonate. Both isomeric crotononitriles are converted by concentrated sulphuric acid into the same (solid) crotonic acid. F. G. M.

Phase Rule Study of the Cupro-, Argento-, Auro-, and Thallo-cyanides of Potassium. H. Bassett and A. S. Corbet (*J. Chem. Soc.*, 1924, **125**, 1660—1675).—The curves obtained for the system KCN–CuCN–H_2O at 25° indicate the existence of four complex cyanides, and these have been isolated. $KCu_2(CN)_3,H_2O$, monoclinic scales, was prepared in small quantity by boiling an excess of cuprous cyanide with 10% aqueous solution of potassium cyanide; on concentrating the mother-liquor, there were first deposited crystals (hexagonal plates or needles) of $KCu(CN)_2$, and, later, prismatic crystals of $K_3Cu(CN)_4$. Colourless rhombohedral crystals of the compound $K_3Cu(CN)_4,H_2O$ were obtained by evaporating a solution containing potassium and cuprous cyanides in the molecular ratio of 3 : 1.

In the system KCN–AgCN–H_2O at 25°, the compounds $KAg(CN)_2$, $K_3Ag(CN)_4,H_2O$, and $KAg_2(CN)_3,H_2O$ can exist in contact with the solution. The *complex*, $K_3Ag(CN)_4,H_2O$, was obtained as large, colourless, tabular prisms on evaporating a solution containing potassium and silver cyanides in the ratio 3 : 1. The *salt*, $KAg_2(CN)_3,H_2O$, forms minute needles.

No evidence was obtained for the existence of potassium aurocyanides other than $KAu(CN)_2$. One thallocyanide, $KTl(CN)_2,H_2O$ (rectangular prisms), is capable of existence in the system KCN–TlCN–H_2O. C. J. S.

Decomposition of the Octacyanides of Quadrivalent Molybdenum and Tungsten by Sunlight. I. O. COLLENBERG (*Z. anorg. Chem.*, 1924, **136**, 245—251).—Sulphuric acid solutions of compounds of the type $K_4R(CN)_8$, where R=Mo or W, are pale yellow in colour, but, on exposure to bright sunlight, they turn, in succession, reddish-brown, dark brown, and eventually green, whilst a brown, flocculent precipitate forms. No definite compounds could be isolated from the decomposed solution. The corresponding octacyanides in *N*-potassium hydroxide solution undergo a change on exposure to bright sunlight involving the replacement of four cyano groups successively by hydroxyl, and the colour of the solution passes through brown to violet. From the violet solutions addition of excess of potassium hydroxide precipitates, in the cold, crystalline substances having the composition

$$K_4[R(OH)_3(CN)_5],xH_2O.$$

The tungsten compound is yellowish-brown in colour and gives violet solutions. The molybdenum compound exists in two forms, one, yellow-brown in colour, crystallising from hot solutions, and the other, reddish-violet in colour, from cold; both give deep blue solutions in water. A. R. P.

Preparation of Hydroxyethylarsinic Acid. LES ÉTABL. POULENC FRÈRES and C. OECHSLIN (Brit. Pat. 206143).—An ethylene dihalide is heated with an aqueous solution of an alkali arsenite; the resulting mixture is neutralised with hydrochloric acid and hydrogen peroxide is added to convert any free arsenious into arsenic acid, which is removed with magnesium oxide.

W. T. K. B.

Preparation of Magnesium Methyl Chloride for the Grignard Reaction. H. SCHMALFUSS (*J. pr. Chem.*, 1924, [ii], **108**, 88—90).—The reaction between magnesium and gaseous methyl chloride is greatly accelerated by a catalyst formed by mixing in a flask the magnesium, some ethyl bromide, a few crystals of iodine, and a very little ether. The catalyst is formed at once, dry ether is added, and a stream of dry methyl chloride gas is passed into the boiling ether as fast as it can be absorbed. Using the magnesium methyl chloride thus prepared, 98% of the theoretical yield of diphenylmethylcarbinol was obtained from benzophenone.

E. H. R.

Valency Requirements of Organic Radicals. K. von Auwers (*Ber.*, 1924, **57**, [*B*], 1051—1056).—A theoretical survey of results obtained by Meerwein (A., 1920, i, 2; this vol., i, 188, 191), von Braun (A., 1923, i, 1193; this vol., i, 632), Skraup (A., 1919, i, 598), Steinkopf (A., 1922, i, 994), and Schonberg (this vol., i, 520) in relation to observations of the author and Zincke on ψ-phenols (A., 1900, i, 159), *p*-hydroxybenzylpiperidines (A., 1906, i, 258), phenyl benzyl ethers (A., 1900, i, 168; 1902, i, 212; 1906, i, 347; 1907, i, 1033), *o*- and *p*-hydroxybenzyl bromides (A., 1900, i, 154), and *pp'*-dihydroxydiphenylmethanes (A., 1906, i, 263; 1907, i, 919). The relative tenacity of the radicals is not under all conditions a measure of their valency requirements, since other factors, such as steric hindrance and ionisation, may come into play. R. B.

Isomerisation due to the Action of Zinc Dust and Alcohol on the Stereoisomeric Dibromodimethyl*cyclo*hexanes. A. Uspenski (*Trans. Inst. Chem. Reagents, Moscow*, 1923, No. 2, 5—9).—When the solid *cis*-3 : 5-dibromo-1 : 1-dimethyl*cyclo*hexane (A., 1923, i, 666) is reduced by means of zinc dust and alcohol, the product is the pure bicyclic hydrocarbon (*loc. cit.*), b. p. 114—114·1°/740 mm., d_4^{20} 0·8131, n_D^{20} 1·4350; if the liquid isomeride, consisting mainly of the *trans*-form, is employed a mixture is obtained, b. p. 115·5°/740 mm., d_4^{20} 0·7885, n_D^{20} 1·4337, which contains only small quantities of the above hydrocarbon, the greater part consisting of the unsaturated isomeride, as evidenced by the high molecular refractivity and its reaction with permanganate. G. A. R. K.

Refractive Index of Benzene and Carbon Tetrachloride in an Electric Field. Pauthenier.—(See ii, 582.)

Sulphonation of Benzene. A. W. Harvey and G. Stegeman (*Ind. Eng. Chem.*, 1924, **16**, 842—845).—When benzene vapour is passed through sulphuric acid (93·2%) at 130—170°, the concentration of the sulphuric acid falls, first rapidly, then more slowly, until a limiting value (0·6% at 170°) is reached. The concentration of benzenesulphonic acid shows a corresponding increase, but reaches a maximum (88—92%) before the limiting sulphuric acid concentration is attained. This point corresponds with the commencement of the formation of diphenylsulphone, according to the equations $2PhSO_3H=Ph_2SO_2+H_2SO_4$, and $PhSO_3H+C_6H_6=Ph_2SO_2+H_2O$. As the sulphone does not appear until the concentration of sulphuric acid has fallen below 10%, its production by the direct action of benzene on sulphuric acid appears to be excluded. F. G. W.

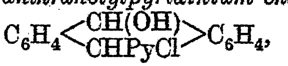
Special Examples of Grignard's Reaction. H. Goudet and H. Paillard (*Helv. Chim. Acta*, 1924, **7**, 638—640).—β-Phthalimidoethyl bromide (ω-bromoethylphthalimide) interacts with magnesium phenyl bromide to form a compound which when treated with water yields 3-*hydroxy*-3-*phenyl*-2-β-*bromoethyl*iso*indolinone*, colourless needles, m. p. 179·5—180·5°. This product will not react further with a Grignard reagent (cf. Sachs and Ludwig, A., 1904, i, 266), nor will the intermediate magnesium complex interact with magnesium. The magnesium complex obtained by treating β-bromoethylamine with magnesium ethyl bromide will not react with magnesium.

Monochloroacetone is not affected by magnesium but methyl α-chloroethyl ketone undergoes reaction, provided the magnesium is previously amalgamated and some ethyl bromide is used to start the reaction. With *cyclo*hexanone as medium a poor yield of 1-β-*acetylethyl*cyclo*hexan*-1-*ol*, m. p. 123—124°, is obtained. W. A. S.

o-Chlorodinitrotoluenes. V. 2-Chloro-3 : 6-dinitrotoluene. G. T. Morgan and T. Glover (*J. Chem. Soc.*, 1924, **125**, 1597—1601).—The completion of the set of six 2-chlorodinitrotoluenes demanded by theory is realised in the synthesis of 2-chloro-3 : 6-dinitrotoluene. By the action of toluene-*p*-sulphonyl chloride on 6-chloro-*o*-toluidine, 6-*chlorotoluene*-p-*sulphonyl*-o-*toluidide* was obtained, prisms, m. p. 119°, giving when nitrated 6-*chloro*-5-*nitrotoluene*-p-*sulphonyl*-o-*toluidide*, m. p. 157°. Hydrolysis of this gave 6-*chloro*-5-*nitro*-o-*toluidine* (m. p. 162°), which was oxidised by Caro's acid in the cold. 2-*Chloro*-3 : 6-*dinitrotoluene* forms long, colourless needles, m. p. 61·5—63°. 6-*Chloro*-2 : 5-*tolylenediamine*, m. p. 89—90°, was obtained by reducing an alcoholic solution of 6-chloro-5-nitro-*o*-toluidine by means of zinc dust and ammonium chloride. Nitration of 6-chloroaceto-*o*-toluidide gave chiefly 6-chloro-3-nitroaceto-*o*-toluidide, identified by hydrolysis to 6-chloro-3-nitro-*o*-toluidine. W. E. E.

Studies in Chemical Reactivity. II. The Anthracene $\rightleftharpoons$ Dianthracene Reaction, Photochemical and Thermal. H. A. Taylor and W. C. McC. Lewis.—(See ii, 580.)

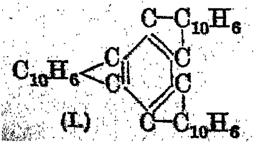
Anthracene Derivative. Badische Anilin- und Soda-Fabrik and H. Hopff (D.R.-P. 381180; from *Chem. Zentr.*, 1924, i, 1446).—The following compounds, obtained from the chlorination of anthracene in the presence of pyridine, are mentioned : 9 : 10-*dihydroanthracenedipyridinium chloride*, $C_6H_4{<}{\substack{CHPyCl \\ CHPyCl}}{>}C_6H_4$, crystals, m. p. 180°; *anthranolylpyridinium chloride*,



$$C_6H_4{<}{\substack{CH(OH) \\ CHPyCl}}{>}C_6H_4,$$

a brown substance. G. W. R.

Decacyclene. I. Reduction of Decacyclene. K. Dziewoński and J. Suszko (*Bull. Acad. Polon. Sci. Lett.*, 1923, [*A*], 17—24; from *Chem. Zentr.*, 1924, i, 1377—1378).—By reduction of decacyclene (trinaphthylenebenzene, annexed formula) with hydriodic acid and red phosphorus the following compounds are obtained : *hexahydrodecacyclene*, $C_{36}H_{24}$, a brown, amorphous mass, m. p. 355—365°; *octahydrodecacyclene*, $C_{36}H_{26}$, an amorphous, reddish-brown mass, m. p. 300—310°; *dodecahydrodecacyclene*, $C_{36}H_{30}$, dark red, microcrystalline, m. p. 255°; *hexadecahydrodecacyclene*, $C_{36}H_{34}$, orange-yellow, microcrystalline, m. p.



(I.)

150—160°; *octadecahydrodecacyclene*, $C_{36}H_{36}$, yellow, microcrystalline, m. p. 125—128°; *hexaeikosihydrodecacyclene*, $C_{36}H_{44}$, light yellow oil, b. p. 330—340°/10—12 mm. Structural formulæ, showing hydrogenation by stages of the naphthylene residues, are given for each of the reduction products. G. W. R.

***cyclo*Hexylamines.** Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 382714; from *Chem. Zentr.*, 1924, i, 1592).—*cyclo*Hexylamines are prepared by heating *cyclo*hexanol with primary or secondary amines or their substitution products and zinc chloride. cyclo*Hexylaniline* is an oil, b. p. 130°/4 mm.; N-cyclo*hexyl*-m-*toluidine*, b. p. 155—160°/13 mm.; N-cyclo*hexylethyl*-o-*toluidine*, an oil, b. p. 175°/22 mm. G. W. R.

Reactions of Thiocarbonyl Chloride. I. Reaction with Aromatic Primary Amino Compounds. G. M. Dyson and H. J. George (*J. Chem. Soc.*, 1924, **125**, 1702—1708).—When an aromatic amine is substituted in the nucleus by a halogen, nitro, or hydroxyl group, the Hofmann method of preparing symmetrically disubstituted thiocarbamides is unsatisfactory. A general method of preparing this type of compound is described, based on the action of thiocarbonyl chloride on aniline, by which phenylthiocarbimide is obtained. The presence of a single halogen atom, hydroxyl, alkoxyl, or carbethoxyl group does not lessen the activity of the amine; the presence of a nitro group increases its activity. Thiocarbimides are obtained when equal weights of thiocarbonyl chloride and amine are used and thiocarbamides when the amine is in excess. The following new compounds are described:—3 : 4-*dimethylphenylthiocarbimide*, pale yellow oil, b. p. 263—264°; 3 : 4-*dimethylphenylthiocarbamide*, by the action of boiling aqueous alcoholic ammonia on the preceding compound, m. p. 141·5—142·5°; s-*di*-3 : 4-*dimethylphenylthiocarbamide*, m. p. 178·5—179°; 2 : 4-*dimethylphenylthiocarbimide*, m. p. 28—29°; 2 : 4-*dimethylphenylthiocarbamide*, m. p. 181·5°; s-*di*-2 : 4-*dimethylphenylthiocarbamide*, m. p. 149—150°; 2 : 5-*dimethylphenylthiocarbimide*, a pale, straw-coloured oil, b. p. 262—263°; 2 : 5-*dimethylphenylthiocarbamide*, m. p. 134·5—135·5°; s-*di*-2 : 5-*dimethylphenylthiocarbamide*, m. p. 148—148·5°; *ψ-cumidylthiocarbimide*, m. p. 22—23°; *ψ-cumidylthiocarbamide*, m. p. 167·5—168°; s-*di-ψ-cumidylthiocarbamide*, m. p. 145—146·5°; 5-*bromo*-o-*tolylthiocarbimide*, m. p. 48—49°; 5-*bromo*-o-*tolylthiocarbamide*, m. p. 186°; s-*di*-5-*bromo*-o-*tolylthiocarbamide*, m. p. 159°; p-*nitrophenylthiocarbamide*, m. p. 189—190°; 5-*nitro*-o-*tolylthiocarbimide*, m. p. 55—56°; 5-*nitro*-o-*tolylthiocarbamide*, m. p. 188·5°; s-*di*-5-*nitro*-o-*tolylthiocarbamide*, m. p. 130—131°; *nitromesitylthiocarbimide*, pale yellow, hair-like crystals, m. p. 74—75°; s-*di*-(*nitromesityl*)*thiocarbamide*, m. p. 244°; *nitromesitylthiocarbamide*, m. p. 199°; m-*hydroxyphenylthiocarbamide*, m. p. 287° (decomp.); p-*anisylthiocarbamide*, m. p. 210—211°; p-*phenetylthiocarbimide*, m. p. 75—76°; p-*phenetylthiocarbamide*, m. p. 175—176°; s-*di*-p-*phenetylthiocarbamide*, m. p. 171°; o-*carbethoxyphenylthiocarbimide*, yellow oil, b. p. 288—290° (slight decomp.); o-*carbethoxyphenylthiocarbamide*, m. p. 306—308°; s-*di*-o-*carbethoxyphenylthiocarbamide*, decomp. before melting.

W. E. E.

Halogen-substituted Arylthiocarbimides. F. D. CHATTAWAY, R. K. HARDY, and H. G. WATTS (*J. Chem. Soc.*, 1924, **125**, 1552—1555).—In Hofmann's method of preparing thiocarbimides, the yield of the intermediate carbamide and also that of the final product depend on the nature of the substituents in the aromatic nucleus. Whereas aniline and *o*- and *p*-toluidine react readily with carbon disulphide, their monohalogen derivatives are much less active and their dihalogen derivatives almost inert. When a thiocarbamide, obtained by the addition of phenylthiocarbimide to a halogen-substituted arylamine, is hydrolysed by acid, the more basic unsubstituted residue is removed and a halogen-substituted arylthiocarbimide is produced.

p-*Chlorophenylthiocarbimide*, crystals, m. p. 44·5°, warmed with concentrated aqueous ammonia, gives the corresponding *carbamide*, m. p. 178°. 2 : 4-*Dichlorophenylthiocarbimide*, m. p. 39°, b. p. 208°/17·5 mm. 2 : 4-*Dichlorophenylthiocarbamide*, m. p. 158°. Methyl dichlorophenylthiocarbamate, m. p. 48·5°; corresponding *ethyl* and n-*propyl* esters, m. p. 79° and 72°, respectively. 2 : 4-*Dibromophenylthiocarbimide*, m. p. 59·5°; corresponding *carbamide*, m. p. 170°. *Ethyl* 2 : 4-*dibromophenylthiocarbamate*, m. p. 62°; corresponding n-*propyl* ester, m. p. 68°. n-*Butyl phenylthiocarbamate*, m. p. 55°; n-*butyl* p-*tolylthiocarbamate*, m. p. 65°. p-*Chlorophenyl*-p-*tolylthiocarbamide*, m. p. 173°; p-*chlorophenyl*-o-*tolylthiocarbamide*, m. p. 119·5°; p-*bromophenyl*-p-*tolylthiocarbamide*, m. p. 182°; 2 : 4-*dichlorodiphenylthiocarbamide*, m. p. 157°; 2 : 4-*dibromodiphenylthiocarbamide*, m. p. 165°; 2 : 4-*dichlorophenyl*-p-*tolylthiocarbamide*, m. p. 145°.

W. E. E.

Some Binary Systems composed of Acetic Acid and the Homologues of Aniline. E. A. O'CONNOR (*J. Chem. Soc.*, 1924, **125**, 1422—1427; cf. T., 1921, **119**, 401).—The solid additive compounds formed on mixing certain amines with glacial acetic acid have been isolated and the composition of the liquid phases in equilibrium with these solids determined for various temperatures. *o*-Toluidine forms a *compound*, $C_7H_7{\cdot}NH_2,C_2H_4O_2$, m. p. 24·8°, deposited over a large range of composition. *m*-Toluidine forms a compound, $C_7H_7{\cdot}NH_2,2C_2H_4O_2$, existing as a stable α-form, m. p. 10·0°, and a metastable or β-form, m. p. 7·3°. The β-form was metastable to the α-form throughout the range investigated, but no definite conditions for their separation were discovered. The invariant points α- and β-$C_7H_7{\cdot}NH_2,2C_2H_4O_2$–$C_7H_7{\cdot}NH_2$–liquid lie at −37·7° and 13% and −39·0° and 16·0% acetic acid, respectively. *p*-Toluidine forms $C_7H_7{\cdot}NH_2,2C_2H_4O_2$, m. p. 48·0°; mesidine forms $C_9H_{11}{\cdot}NH_2,C_2H_4O_2$, m. p. 18·9°. Dimethylaniline forms no compound with acetic acid as a solid phase; the heat evolution is extremely small, whilst the complexes of the tertiary amine and acid lack the viscosity at low temperatures characteristic of the primary amines. Combination obviously takes place in the case of monomethylaniline but no solid phase could be induced to separate. The ratio 1 amine : 1 acid appears to hold where the primary amine possesses a methyl group in the ortho-position; where this is not the case the ratio is 1 amine : 2 acid. The type $2C_6H_5{\cdot}NH_2,C_2H_4O$ seems to be peculiar to aniline.

A. C.

Derivatives of Naphthylaminesulphonic Acids and Aminonaphtholsulphonic Acids. CHEM. FABR. VORM. WEILER-TER MEER and H. SUIDA (D.R.-P. 380578; Austr. Pat. 93324; from *Chem. Zentr.*, 1924, i, 1593—1594).—The patent describes the preparation of colouring matters containing sulphur by the action of sulphur monochloride on salts of naphthylaminesulphonic acids and aminonaphtholsulphonic acids. G. W. R.

Monoiodo Derivatives of *o*-Nitrophenol. I. S. KEIMATSU (*J. Pharm. Soc. Japan*, 1924, No. 507, 319—326).—Hübner's α- and β-iodonitrophenols (*Ber.*, 1874, 7, 462) are stated to be the 5- and 6-iodo-2-nitrophenols (cf. Beilstein, II, 700). By heating 3-nitro-4-hydroxyphenylarsinic acid (4 g.) with potassium iodide (8 g.) in water (56 c.c.), 5*N*-sulphuric acid (16 c.c.), and alcohol (10 c.c.) during 3 hours, 4-iodo-2-nitrophenol, m. p. 80—81°, is obtained (cf. Roberts, T., 1923, **123**, 2707). When the nitration product, m. p. 214—218°, of *o*-hydroxyphenylarsinic acid (probably a mixture of at least two nitro compounds) is treated with potassium iodide and sulphuric acid as above, a mixture of 6-iodo-2-nitrophenol (obtained by Brenans by the nitration of *o*-iodophenol), and 2-iodo-4-nitrophenol is obtained. It is concluded that Hübner's α- and β-compounds are the 3- and 4-iodo derivatives. K. K.

Derivatives of 2 : 6-Dinitrophenol. E. FROMM and R. EBERT (*J. pr. Chem.*, 1924, [ii], **108**, 75—87).—2 : 6-*Dinitrophenyl benzoate* forms flat needles, m. p. 112°. Bromination of 2 : 6-dinitrophenol in alcohol gives 4-*bromo*-2 : 6-*dinitrophenol*, m. p. 78°; *benzoate*, m. p. 154°; 4-*bromo*-2 : 6-*dinitroanisole* has m. p. 88°. By the action of benzoyl chloride on 2 : 6-diaminophenol hydrochloride is formed 6-*benzamido*-2-*phenylbenzoxazole*, m. p. 222°, and some 2 : 6-*dibenzamidophenol*, m. p. 181°; *benzoate*, m. p. 220°. 2 : 6-*Diacetamidophenol* has m. p. 165°, and its *acetate*, m. p. 224°; *tetra-acetyl*-2 : 6-*diaminophenyl acetate*, m. p. 167°. 6-*Acetamido*-2-*methylbenzoxazole*, obtained by heating 2 : 6-diacetamidophenyl acetate at 230—235°, has m. p. 148°.

2 : 6-*Diaminophenyl* p-*toluenesulphonate* has m. p. 141°; *dibenzoyl* derivative, m. p. 191°; 2 : 6-*di*-p-*toluenesulphonamidophenol*, m. p. 190°.

2 : 6-*Diaminoanisole dihydrochloride* was obtained by reduction of 2 : 6-dinitroanisole; the following derivatives of the base were obtained: *dibenzoyl*, m. p. 157°; *diacetyl*, m. p. 222°; di-p-*toluenesulphonyl*, m. p. 185°. 2 : 6-*Diaminophenetole dihydrochloride* was prepared; 2 : 6-*diacetamidophenetole* has m. p. 240°.

2 : 6-*Diamino*-p-*cresol dihydrochloride* is described; 2 : 6-*diacetamido*-p-*cresol* has m. p. 225—227°; *acetate*, m. p. 228°.

Oxidation of 2 : 6-diacetamidophenol with ferric chloride gives 3 : 5 : 3′ : 5′-*tetra-acetamidodiphenoquinone*, a dark blue, crystalline precipitate, which is reduced by hyposulphite to 3 : 5 : 3′ : 5′-*tetra-acetamido*-4 : 4′-*dihydroxydiphenyl*. With formaldehyde, 2 : 6-diaminophenol forms a *compound*, $C_8H_{10}O_2N_2,2HCl$.

2 : 3 : 6-*Tribenzamidoanisole*, m. p. 225—226°, is obtained by coupling diazobenzene-*p*-sulphonic acid with 2 : 6-diaminoanisole, reducing the azo dye, and benzoylating the resulting triaminoanisole. The last forms with benzil a *quinoxaline* derivative, giving a *hydrochloride*, $C_{21}H_{18}ON_3Cl$, bright red needles. E. H. R.

Chromammines. I. Salts of Nitro and other Dyes. H. J. S. King (*J. Chem. Soc.*, 1924, **125**, 1329—1337).—Dyes containing chelate groups, as those of the quinoneoxime, alizarin, and azosalicylic acid series, readily displace ammonia from the chromammine complex. The chloropentammino- and hexamminochromic salts of the nitro dyes picric acid, aurantia, naphthol-yellow N and S, resemble those obtained from the cobaltammines (T., 1922, **121**, 1723); on boiling they liberate 3 ammonia molecules in about 20 minutes, with precipitation of chromic hydroxide and formation of the ammonium salt of the dye, a reaction which differentiates them from compounds containing chelate groups. It was not found possible to prepare normal hexamminochromic alizarinate, the mono-salt being obtained. Hexamminochromic picramate contains no chelate grouping, possibly indicating that picramic acid has a *p*-quinonoid structure. The alkaline solution obtained from aquopentamminocobaltic chloride and moist silver oxide reacts with naphthol-yellow S as if containing hydroxopentamminocobaltic hydroxide. A. Cousen.

Derivatives of *para*-Substituted Phenylcarbamides. C. F. Boehringer u. Söhne G.m.b.H., L. Ach, and A. Rothmann (D.R.-P. 377816 and 377817; from *Chem. Zentr.*, 1924, i, 964; cf. A., 1923, i, 948).—as-p-*Hydroxyphenylmethylcarbamide*, $N(C_6H_4OH)Me{\cdot}CO{\cdot}NH_2$, forms needles, m. p. 175°; as-p-β-*hydroxyethoxyphenylmethylcarbamide*, $N(C_6H_4{\cdot}O{\cdot}C_2H_4OH)Me{\cdot}CO{\cdot}NH_2$, forms needles, m. p. 140—141°. G. W. R.

Electrochemical Oxidation of the three Tolyl Methyl Ethers. F. Fichter and H. Ris (*Helv. Chim. Acta*, 1924, **7**, 803—813; cf. this vol., i, 282, 629).—Anodic oxidation of *p*-tolyl methyl ether gives methyl alcohol, anisaldehyde, anisic acid, 2-*hydroxy*-2′-*methoxy*-5 : 5′-*dimethyldiphenyl*, an oil, b. p. 205°/12 mm., and 2 : 2′-*dimethoxy*-5 : 5′-*dimethyldiphenyl*, m. p. 71°, b. p. 188°/12 mm. (also prepared by methylating the corresponding diphenol), together with unidentified products of high b. p. The constitution of Fichter and Ackermann's 2 : 2′-dihydroxy-5 : 5′-dimethyldiphenyl (A., 1919, i, 586) was verified by preparing it from *o*-tolidinedisulphonic acid; it yields a *dibenzoyl* derivative, m. p. 136°. Anisaldehyde is converted by anodic oxidation, using a platinum anode, into anisic acid. The oxidation of *p*-tolyl methyl ether in the nucleus, not in the side-chain to anisic acid, is favoured by high current density, and by using a weak acid and a platinum anode. *m*-Tolyl methyl ether suffers no attack in the side-chain, but is converted into toluquinol (by cathodic reduction of the quinone formed by oxidation), toluquinone, and *4-hydroxy-4'-methoxy-2 : 2'-dimethyldiphenyl*, b. p. 230—235°/12 mm. *o*-Tolyl methyl ether yields methyl alcohol, toluquinol, and a viscous oil, b. p. 190—280°/12 mm., the relative amount of which increases when a higher current density or a platinum anode is used; this appears to be chiefly *4-hydroxy-4'-methoxy-3 : 3'-dimethyldiphenyl*, and gives the corresponding diphenol on demethylation. Toluquinol is oxidised, in cold acetic acid solution containing sulphuric acid, to ditolyldiquinone; its dimethyl ether to 2 : 2' : 5 : 5'-tetramethoxy-4 : 4'-dimethyldiphenyl, and a quinone (cf. Nietzki and Bernard, A., 1898, i, 529). W. A. S.

***o*-Hydroxydiphenyl.** K. von Auwers and G. Wittig (*J. pr. Chem.*, 1924, [ii], **108**, 99—112).—The reactions of *o*-hydroxydiphenyl are in general similar to those of *o*-cresol. Bromination in acetic acid gives an oily mixture of monobromo derivatives, *3 : 5-dibromo-2-hydroxydiphenyl*, m. p. 56—57°, and *3 : 5 : 4'-tribromo-2-hydroxydiphenyl*, m. p. 151—152° (*methyl ether*, m. p. 98—98·5°, *benzoate*, m. p. 132—133°). By 2*N*-sodium hydroxide the tribromo derivative is converted into a red, amorphous substance.

o-Hydroxydiphenyl reacts slowly with formaldehyde in the cold to form *2-hydroxy-3 : 5-dihydroxymethyldiphenyl*, m. p. 124·5°, which with hydrogen bromide in acetic acid forms *2-hydroxy-3 : 5-dibromomethyldiphenyl*, m. p. 100·5—101°. By the Friedel-Crafts reaction, *o*-diphenyl methyl ether gives *5-acetyl-o-diphenyl methyl ether*, m. p. 91·5—92°; *semicarbazone*, m. p. 209—210°. By heating *o*-hydroxydiphenyl acetate at 130° with aluminium chloride, a mixture of *2-hydroxy-5-acetyldiphenyl* (m. p. 172—173°; *semicarbazone*, m. p. 213°) and *2-hydroxy-3-acetyldiphenyl* (m. p. 60—61°; *semicarbazone*, m. p. 214—215°; *oxime*, m. p. 165—166°) is obtained. *2-Hydroxy-5-ethyldiphenyl* is a pale yellow oil, b. p. 171—172°/18 mm.; *phenylurethane*, m. p. 114—115°.

o-*Diphenyl allyl ether*, b. p. 166—167°/12·5 mm., $d_4^{20\cdot9}$ 1·0601, $n_\alpha^{20\cdot9}$ 1·58910, changes at 250—300° into *2-hydroxy-3-allyldiphenyl*, b. p. 176—178°/13 mm., $d_4^{18\cdot7}$ 1·0735, $n_\alpha^{18\cdot7}$ 1·59411; *phenylurethane*, m. p. 124·5—125·5°. The allyl derivative changes when heated with methyl-alcoholic potassium hydroxide into *2-hydroxy-3-propenyldiphenyl*, b. p. 185—187°/13 mm., $d_4^{18\cdot3}$ 1·0897, $n_\alpha^{16\cdot3}$ 1·61994; *phenylurethane*, m. p. 166—167·5°; *methyl ether*, b. p. 173—174°/12 mm. Reduction of the propenyl compound with sodium and alcohol gives *2-hydroxy-3-propyldiphenyl*, b. p. 169—172°/13 mm., d_4^{16} 1·0512, n_α^{16} 1·57462; *phenylurethane*, m. p. 126·5—127·5°. Oxidation of the methyl ether of the propenyl compound with permanganate gives *2-methoxydiphenyl-3-carboxylic acid*, m. p. 119—120°.

o-*Hydroxydiphenyl propionate*, b. p. 168—169°/12 mm., is converted by aluminium chloride into *2-hydroxy-5-propionyldiphenyl*, m. p. 148°. *2-Hydroxy-5-propyldiphenyl* has b. p. 178—179°/12 mm.; *phenylurethane*, m. p. 132—132·5°.

5-*Benzeneazo*-2-*hydroxydiphenyl* has m. p. 95—96° and 3 : 5-*bis-benzeneazo*-2-*hydroxydiphenyl*, m. p. 157°. E. H. R.

Univalent Oxygen. III. 9-Chloro-10-phenanthroxyl. S. Goldschmidt and C. Steigerwald (*Annalen*, 1924, **438**, 202—216; cf. A., 1922, i, 1148, 1149).—9-Chloro-10-hydroxyphenanthrene (Schmidt and Lumpp, A., 1909, i, 34) is oxidised in chloroform solution to 9-*chloro*-10-*phenanthryl peroxide*, a colourless substance, m. p. 124—125° (decomp.). In solution, this compound undergoes dissociation into the free radical, 9-*chloro*-10-*phenanthroxyl*, the dissociation being influenced by the presence of traces of hydrogen chloride and therefore proceeding best when pyridine is present; 69% of the substance may then be present as the free radical. When the original oxidation of the chlorophenanthrol is carried out quickly, as by using potassium ferricyanide in aqueous solution, and the product is immediately extracted with chloroform, the free radical is present to the extent of 10% (determined by titration with hydrazobenzene; cf. Goldschmidt and Wolffhardt, this vol., i, 886). The two substances may be separated by fractionally precipitating the chloroform solution with petrol, the peroxide being first thrown down, and the phenanthroxyl separating later as an amorphous blue deposit. 9-Chloro-10-phenanthroxyl resembles its congeners (*loc. cit.*); it unites with bromine to form a yellow compound in which the bromine must be attached to the oxygen atom. W. A. S.

Mechanism of the Action of Potassium Permanganate on Unsaturated Compounds. S. Nametkin (*J. pr. Chem.*, 1924, [ii], **108**, 46—51).—By the action of potassium permanganate on unsaturated compounds, glycols are formed, but it has never been decided whether these are produced by hydration of primarily formed oxides. It is shown, by reference to *cyclo*hexanediol and some of its homologues, that this cannot be the case, since hydration of the oxide gives a *cis*-glycol whereas oxidation of the *cyclo*hexene with permanganate gives the *trans*-glycol. It is probable that 2 mols. of permanganate participate in the oxidation, forming at the double bond a complex which by hydration gives a glycol and a manganate, the latter quickly decomposing :

$$\begin{array}{l}-\mathrm{CH\cdot O\cdot MnO_2\cdot OK}\\ \quad|\\ -\mathrm{CH\cdot O\cdot MnO_2\cdot OK}\end{array} + 2\mathrm{H_2O} \longrightarrow \begin{array}{l}-\mathrm{CH\cdot OH}\\ \quad|\\ -\mathrm{CH\cdot OH}\end{array} + 2\mathrm{MnO_4HK}.$$

In this way either a *cis*- or *trans*-glycol could be formed, but only the *trans*-isomeride is found. E. H. R.

Molecular Transpositions. Preparation and Dehydration of ααγ-Triphenyl-ββ-dimethylpropan-α-ol. (Mme.) P. Ramart (*Compt. rend.*, 1924, **179**, 276—279).—By the action of magnesium phenyl bromide on benzyldimethylacetophenone, *ααγ-triphenyl-ββ-dimethylpropan-α-ol*, m. p. 100—101°, distilling without decomposition at 280°/25 mm., is obtained. By the action of thionyl chloride on this, *α-chloro-ααγ-triphenyl-ββ-dimethylpropane* is obtained. Dehydration of the alcohol by means of a mixture of acetic anhydride and acetyl chloride yields a mixture of two isomeric *hydrocarbons*, $C_{23}H_{22}$, difficult to separate, m. p. 110° and 89·9° respectively. The latter is converted into the former on treatment with a solution of hydrogen bromide in acetic acid. Dehydration by the action of heat (300—350° at 25 mm.) in the presence of infusorial earth yields *iso*butylbenzene, b. p. 171°, benzophenone, and the hydrocarbon, m. p. 110°. J. W. B.

Application of the Grignard Reaction to some Acetylenic Compounds. II. F. J. WILSON and W. McN. HYSLOP (*J. Chem. Soc.*, 1924, **125**, 1556—1558; cf. *ibid.*, 1923, **123**, 2612).—On heating with sulphuric acid, $\alpha\theta$-diphenyl-$\gamma\zeta$-dimethyl-$\Delta^{\alpha\eta}$-octadiinene-$\gamma\zeta$-diol (α modification) is converted into 2 : 5-*diphenylacetylenyl*-2 : 5-*dimethyltetrahydrofuran*, b. p. 206—207°/0·5 mm. Except for some charring, $\alpha\zeta$-diphenyl-$\gamma\delta$-dimethyl-$\Delta^{\alpha\epsilon}$-hexadiinene-$\gamma\delta$-diol was not affected by this treatment. With sodium hydroxide solution both glycols gave, as the only recognisable product, phenylacetylene. Attempts were made to obtain acetylenic ketols. Diacetyl and magnesium phenylacetylenyl bromide gave *α-phenyl-γ-methyl-Δ^{α}-pentinen-γ-ol-δ-one*, b. p. 120°/0·5 mm. (*semicarbazone*, m. p. 171—172°), together with the glycol previously described. When acetonylacetone was subjected to this reaction, only the glycol was obtained. Two tetra-acetylenic glycols have been prepared: *$\alpha\alpha\beta\beta$-tetraphenylacetylenylethylene glycol* (m. p. 147°) from ethyl oxalate and magnesium phenylacetylenyl bromide, and *$\alpha\alpha\delta\delta$-tetraphenylacetylenyl-$\alpha\delta$-butylene glycol* (m. p. 134—136°) from ethyl succinate and the same Grignard reagent. W. E. E.

Glycol Ethers of certain Aromatic Nitrohydroxy Compounds. O. MATTER (D.R.-P. 379881; from *Chem. Zentr.*, 1924, i, 1103—1104).—p-*Nitrophenyl hydroxyethyl ether*,

$$NO_2{\cdot}C_6H_4{\cdot}O{\cdot}C_2H_4{\cdot}OH,$$

from *p*-chloronitrobenzene and ethylene glycol, has m. p. 96—97°. o-*Nitrophenyl hydroxyethyl ether*, m. p. 37—38°, and 4-*nitronaphthyl hydroxyethyl ether*, m. p. 131—132°, were also prepared.
G. W. R.

Thiophenols. VIII. 5-Chloro-2-methylthioltriphenylcarbinols. K. BRAND and W. GROEBE (*J. pr. Chem.*, 1924, [ii], **108**, 1—18; cf. this vol., i, 852).—By reduction of 4-chloro-2-nitrophenyl methyl sulphide in methyl-alcoholic solution with iron and concentrated hydrochloric acid in presence of copper chloride, *4-chloro-2-aminophenyl methyl sulphide* is obtained, m. p. 29°, b. p. 273—274°, d^{25} 1·2754, n_D^{25} 1·63118; *hydrochloride*, m. p. 198—199°; *nitrate*, unstable, m. p. 148—158°; *sulphate*, m. p. 138—140° (decomp.); *formyl* derivative, m. p. 79—80°; *acetyl* derivative, m. p. 95—96°; *benzoyl* derivative, m. p. 105—106°. Through the diazonium compound (*sulphate*), the amino compound was converted into: *4-chloro-2-bromophenyl methyl sulphide*, m. p. 32—33°; b. p. 140—150°/15 mm.; d^{25} 1·6315; n_D^{16} 1·64223; 2 : 4-*dichlorophenyl methyl sulphide*, b. p. 135—140°/15 mm.; d^{25} 1·3633; n_D^{25} 1·61678; *4-chloro-2-iodophenyl methyl sulphide*, m. p. 26—27°,

b. p. 175—185°/15 mm.; d^{25} 1·881; n_D^{25} 1·6857. When the last was heated with copper bronze at 260—280° it gave 5 : 5′-*dichloro*-2 : 2′-*dimethylthioldiphenyl*, m. p. 160°. 4-*Chloro*-2-*cyanophenyl methyl sulphide*, m. p. 104—105°, is hydrolysed by boiling alcoholic potassium hydroxide to 5-*chloro*-2-*methylthiolbenzoic acid*, m. p. 184—185°; *methyl* ester, m. p. 65—66°. 4-*Chloro*-2-*hydroxyphenyl methyl sulphide* was only obtained in poor yield from the above diazonium sulphate; its *benzoyl* derivative has m. p. 72°.

The magnesium compound of 4-chloro-2-bromophenyl methyl sulphide reacts with benzophenone in presence of a trace of iodine to form 5-*chloro*-2-*methylthioltriphenylcarbinol*, m. p. 111—112°, slightly volatile in steam; the corresponding *chloride* begins to decompose at 114°, m. p. 128°; in concentrated acids the colour is yellowish-green. 5-*Chloro*-2-*methylthioltriphenylmethane* has m. p. 97—98°; with methyl sulphate it forms a *sulphonium methosulphate*, m. p. 186—187°.

Ethyl benzoate reacts with magnesium 5-chloro-2-methylthiolphenyl bromide to form 5 : 5′-*dichloro*-2 : 2′-*dimethylthioltriphenylcarbinol*, m. p. 134—135°; the unstable *chloride* has m. p. 115—126°. 5 : 5′-*Dichloro*-2 : 2′-*dimethylthioltriphenylmethane* has m. p. 120—121°.

From 4-chloro-2-bromophenyl methyl sulphide and methyl 5-chloro-2-methylthiolbenzoate by the Grignard reaction was obtained 5 : 5′ : 5″-*trichloro*-2 : 2′ : 2″-*trimethylthioltriphenylcarbinol*, prisms, m. p. 171—172°, from alcohol and rhombs, m. p. 181—182° from benzene. In a mixture of acetic and sulphuric acids it gives a yellowish-green colour, changing to yellow and then disappearing; the *chloride* reddens at 160°, and has m. p. 170° (decomp.), and the corresponding *triphenylmethane* has m. p. 125—126°. p-*Chlorophenyl methyl sulphide* has b. p. 170°. E. H. R.

Thiophenols. IX. o-Ethylthioltriphenylcarbinols. K. Brand and H. Stein (*J. pr. Chem.*, 1924, [ii], **108**, 19—28).—o-*Nitrophenyl ethyl sulphide*, obtained by reduction of *oo*′-dinitrophenyl disulphide (Brand, A., 1909, i, 855) followed by ethylation of the *o*-nitrophenylmercaptan, has b. p. 172°/10 mm., d^{18} 1·262, n_D^{18} 1·62126. It is reduced by iron and hydrochloric acid (cf. preceding abstract) to o-*aminophenyl ethyl sulphide*, b. p. 144°/15 mm., d^{18} 1·087, n_D^{18} 1·60324. By Sandmeyer's method the last was converted into o-*bromophenyl ethyl sulphide*, b. p. 148°/15 mm., d^{18} 1·4224, n_D^{18} 1·60904; o-*iodophenyl ethyl sulphide*, b. p. 181°/40 mm., d^{18} 1·677, n_D^{18} 1·65687; and o-*cyanophenyl ethyl sulphide*, b. p. 170°/15 mm., d^{18} 1·110, n_D^{18} 1·58570.

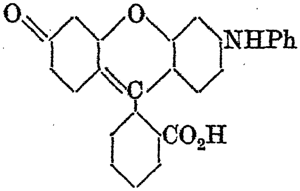
Magnesium *o*-ethylthiolphenyl bromide condenses with benzophenone to give o-*ethylthioltriphenylcarbinol*, m. p. 94°; the corresponding *chloride* has m. p. 117° and o-*ethylthioltriphenylmethane*, m. p. 52°.

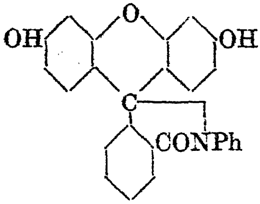
oo′-*Diethylthioltriphenylcarbinol*, m. p. 124°, is obtained by the interaction of the above magnesium compound and ethyl benzoate. The corresponding chloride could not be obtained, but reduction of the carbinol by the method of Kauffmann and Pannwitz (A., 1912, i, 351) gave oo′-*diethylthioltriphenylmethane*, m. p. 98°.

Ethyl o-*ethylthiolbenzoate* has m. p. 28°, b. p. 152°/10 mm., d^{30} 1·118, n^{30}_{D} 1·56309. It reacts with the above magnesium compound to give *oo′o″-triethylthioltriphenylcarbinol,* m. p. 96°; the corresponding *chloride* has m. p. 134°. The colour reactions of the carbinols described are similar to those of the corresponding *o*-methylthiol derivatives (cf. preceding abstract). E. H. R.

Condensation of Fluorescein and Aniline Homologues in Presence of Hydrochloric Acid. T. Maki (*J. Chem. Ind., Japan*, 1924, **27**, 1—15).—When fluorescein (1 mol.) is heated with aniline, *o*- or *p*-toluidine (7 mols.), and hydrochloric acid (1 mol.) at 210°, a mixture of colourless and coloured anilides or toluidides is produced as follows: *fluoresceinanilide,* $C_{26}H_{17}O_4N$, colourless, m. p. 310—311°, and purple, m. p. 311—312°; *fluorescein-*o-*toluidide,* $C_{27}H_{19}O_4N$, colourless, m. p. 323—324°, and red, m. p. 317—318°; and *fluorescein-*p-*toluidide,* $C_{27}H_{19}O_4N$, colourless, m. p. 322—323° (uncor.), and violet, m. p. 333—334° (uncor.). The colourless anilide gives a *diacetyl* derivative, m. p. 252—253°, and the purple one a *monoacetyl* derivative, m. p. 159—160°. The absorption curve and the position of the point of maximum absorption of the purple anilide indicate a quinonoid structure (I) for this isomeride.

(I.)





(II.)

The wave-lengths of the points of maximum absorption of the purple anilide and its homologues are as follows: purple anilide, 5550, red *o*-toluidide, 5330, violet *p*-toluidide, 5570. It is considered that the lactone form of fluorescein is converted into the purple anilide and that the colourless anilide is derived from the quinonoid form of fluorescein. Formula II is suggested for the colourless anilide. K. K.

Preparation of Nitriles from Acid Amides. Farbwerke vorm. Meister, Lucius, und Brüning, E. Schirm, and F. Henle (D.R.-P. 380323; from *Chem. Zentr.*, 1924, i, 1272).—Nitriles are prepared by the action of sulphochlorides of the benzene or naphthalene series on acid amides in the presence of alkali halides or of tertiary bases. Acetonitrile and benzonitrile are prepared from the corresponding amides. G. W. R.

***o*-Aminobenzenecarboxylic Acids.** Kalle u. Co., Akt.-Ges. and M. Schmidt (D.R.-P. 375616; from *Chem. Zentr.*, 1924, i, 966). —*o*-Aminocarboxylic acids are prepared by oxidation of isatin and its derivatives, particularly with hydrogen peroxide in alkaline solution. 5-*Bromo-2-amino-*m-*toluic acid* has m. p. 229°.

G. W. R.

N-Substituted Derivatives of Aminobenzoic Acid. C. F. BOEHRINGER U. SOEHNE G.M.B.H. (Austr. Pat. 94307; Swiss Pat. 101513; from *Chem. Zentr.*, 1924, i, 1595).—The following new compounds are mentioned: N-2-*phenylquinoline*-4-*carboxylanthranilic acid*, $C_9H_5N(Ph)\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H$, m. p. 226—227°; 2-(2′-*carboxyphenylamino*)*quinoline*-4-*carboxylic acid*,

$$CO_2H\cdot C_9H_5N\cdot NH\cdot C_6H_4\cdot CO_2H,$$

m. p. 301° (decomp.), *dimethyl* ester, m. p. 164°; N-2-*phenyl*-6-*methylquinoline*-4-*carboxylanthranilic acid*, m. p. 212°, *methyl* ester, m. p. 155—156°; condensation *compound* from 2-phenylquinoline-4-carboxylic chloride and 4-chloroanthranilic acid; 2-(2′-*carboxy*-4′-*hydroxyphenylamino*)*quinoline*-4-*carboxylic acid*, m. p. about 280°; condensation *compound* from 2-phenylquinoline-4-carboxylic chloride and *p*-aminobenzoic acid, m. p. 282°; the corresponding *compound* with *m*-aminobenzoic acid, m. p. 287°; 2-(3′-*carboxyphenylamino*)*quinoline*-4-*carboxylic acid* and 2-(4′-*carboxyphenylamino*)*quinoline*-4-*carboxylic acid*, m. p. above 305°. G. W. R.

Formula of Anthranil. E. BAMBERGER (*Helv. Chim. Acta*, 1924, 7, 814—815).—Objections are raised (cf. A., 1903, i, 432, etc.) to the "nitrone" formula suggested by Staudinger and Miescher (A., 1919, i, 584). W. A. S.

Catalytic Racemisation of the Diastereoisomeric *l*-Menthyl Phenylbromoacetates. A. MCKENZIE and I. A. SMITH (*J. Chem. Soc.*, 1924, **125**, 1582—1593; cf. *ibid.*, 1923, **123**, 1962).—The production of *l*-menthyl αα-phenylbromoacetate in the esterification of *l*-phenylbromoacetic acid by *l*-menthol in the presence of hydrogen chloride shows that *l*-phenylbromoacetic acid is catalytically racemised by hydrogen chloride; *l*-menthol + *l*-phenylbromoacetic acid ⟶ *l*-menthyl *l*-phenylbromoacetate + *l*-menthyl *d*-phenylbromoacetate. Crystallisation of the mixture gives the *d*-isomeride. When heated with alcoholic hydrogen chloride, the *d*-ester racemises to a mixture of *d*- and *l*-esters, in which the *l*-ester slightly predominates. When esterified in the presence of sulphuric acid, the *d*-acid gives *d*-ester. One or two drops of alcoholic alkali produce catalytic racemisation, the rate of which is greater in the case of *d*-ester than in the case of *l*-ester. Moreover, notably in the case of *l*-menthyl *d*-phenylchloroacetate, the proportions of the two optical isomerides at the end of the racemisation were not equal. The cause of this can be ascribed to the directive influence of the asymmetrical *l*-menthyl group. The following compounds are described:—l-*Menthyl* d-*phenylbromoacetate*, m. p. 78—79°, $[\alpha]_D^{18}+9{\cdot}4°$, $[\alpha]_{5461}^{18}+13{\cdot}2°$ in ethyl alcohol. l-*Menthyl* l-*phenylbromoacetate*, m. p. 40—41°, $[\alpha]_D^{15}-146{\cdot}1°$, $[\alpha]_{5461}^{15}-172{\cdot}8°$ in ethyl alcohol; $[\alpha]_D^{17}-139{\cdot}8°$, $[\alpha]_{5461}^{17}-166{\cdot}9°$ in benzene. *l*-Phenylbromoacetic acid has $[\alpha]_D^{14}-147{\cdot}7°$ in benzene. W. E. E.

Constitution of Curcumone from Curcuma [Turmeric] Oil. H. RUPE and F. WIEDERKEHR (*Helv. Chim. Acta*, 1924, 7, 654—669; cf. A., 1911, i, 293).—When curcuma oil is treated with ozone an acid is obtained which is now shown to be identical with (not, as was at first supposed, different from) curcumic acid, $C_{11}H_{14}O_2$. The latter has m. p. 42—43°, b. p. 163—164°/10 mm., $[\alpha]_D^{20}+46\cdot53°$ or $+47\cdot58°$ according to the method of preparation. Its *ethyl* ester has b. p. 133—134°/10 mm.; the *calcium* and *silver* salts of the acid are described.

p-Tolyl methyl ketone reacts with ethyl bromoacetate and zinc to give a mixture of esters (b. p. 150—153°/9 mm.) which, when hydrolysed by alcoholic potassium hydroxide yields chiefly p-*tolyl-Δ^α-butenoic acid*, needles, m. p. 135°, together with a little β-hydroxy-β-*p*-tolylbutyric acid. *Ethyl* p-*tolyl-Δ^α-butenoate* has b. p. 145—156°/10 mm. When *p*-tolyl-Δ^α-butenoic acid is reduced with hydrogen and a nickel catalyst, β-p-*tolylbutyric acid*, $C_{11}H_{14}O_2$, m. p. 91°, b. p. 165°/10 mm., is formed; its *chloride* has b. p. 125°/9 mm.; the *p-toluidide*, m. p. 112—113°, the *ethyl* ester, b. p. 133—135°/10 mm., and the *calcium* salt are described. This synthetic acid has the same b. p. as curcumic acid; the esters also resemble one another. Only in m. p. and optical activity do the two acids differ. They give similar products when oxidised with cold dilute potassium permanganate solution: curcumic acid yields *p*-tolyl methyl ketone and an optically active dibasic *acid*, $C_{11}H_{12}O_4$, m. p. 227—229°, $[\alpha]_D^{20}+35\cdot34°$, whilst the synthetic acid yields *p*-tolyl methyl ketone and an optically inactive acid of the same composition and m. p. (226°), presumably β-p-*carboxyphenylbutyric acid*. A mixture of the two acids has m. p. 225—227°. Curcumic acid is thus proved to be *d*-β-*p*-tolylbutyric acid.

β-*p*-Tolylbutyryl chloride and zinc methyl yield β-p-*tolylpropyl methyl ketone*, $Me\cdot C_6H_4\cdot CHMe\cdot CH_2\cdot CO\cdot Me$, b. p. 130·5°/11 mm., d_4^{20} 0·9598; *oxime*, b. p. 165—166°/13 mm., *semicarbazone*, m. p. 145—146°, *azine*, b. p. 245—246°/11 mm., *benzylidene* derivative, m. p. 88°. Curcumone has b. p. 130°/11 mm., d_4^{20} 0·9618; it yields an optically active *oxime*, b. p. 165—166°/13 mm., a *semicarbazone*, m. p. 121°, an optically active *azine*, b. p. 245—246°/11 mm., and a *benzylidene* derivative, m. p. 106°. Curcumone is therefore *d*-β-*p*-tolylpropyl methyl ketone.

Before the true nature of the acid obtained by ozonising curcuma oil was discovered attempts were made to reproduce it synthetically. When *p*-tolylacetonitrile is treated in ethereal solution with sodamide followed by methyl iodide, it affords the nitrile of *p*-methylhydratropic acid (b. p. 123°/12·5 mm.; cf. Errera, A., 1892, 605) which, on hydrolysis, yields p-*methylhydratropic acid*, m. p. 34°, b. p. 161—161·5°/12·5 mm., *chloride*, b. p. 122—123°/13·5 mm., *amide*, m. p. 195°, p-*toluidide*, m. p. 102—103°. The latter is accompanied by a little p-*tolylaceto*-p-*toluidide*, m. p. 163°, and after purification serves as a convenient source of pure samples of the parent acid. *Ethyl* p-*methylhydratropate* has b. p. 123·5°/11 mm. Similarly, by using ethyl iodide in the first reaction, α-p-*tolylbutyric acid*, m. p. 67—68°, b. p. 160—161°/11 mm., is prepared, *via* its *nitrile*, b. p. 135°/14 mm. The *chloride* has b. p. 118—120°/12 mm., the *amide* m. p. 105°, the p-*toluidide* m. p. 118°; the *methyl* ester (b. p. 123°/10 mm.), the *ethyl* ester (b. p. 130°/11·5 mm.), and the *magnesium* salt also are described.

W. A. S.

Acid Constituents of the Gum of the Aleppo Pine. I. α- and β-Alepic Acids. G. Dupont (*Bull. Soc. chim.*, 1924, [iv], **35**, 879—889).—The gum is separated by compression into solid and liquid constituents. By dissolving the dry solid in the minimum amount of cold ethyl alcohol and fractionally precipitating with water, samples are obtained which on rapid recrystallisation from cold acetone give a mixture of crystals of two isomeric acids, $C_{20}H_{30}O_2$, termed α- and β-alepic acids. The crystalline forms of the two acids are distinct. *α-Alepic acid* forms orthorhombic prisms, m. p. 148°, $[\alpha]_D-66^\circ$; *β-alepic acid* forms clinorhombic prisms, m. p. 157—159°, $[\alpha]_D-66{\cdot}8^\circ$. Both acids are easily isomerised to α-abietic acid, expecially in alcoholic solution in presence of a trace of hydrochloric acid. The rotatory power of the α-acid falls to $[\alpha]_D-12{\cdot}4^\circ$ and then rises to $[\alpha]_D-84{\cdot}4^\circ$, whereas the minimum value shown by the β-acid under these conditions is $[\alpha]_D-55{\cdot}0^\circ$, rising finally to $[\alpha]_D-86{\cdot}0^\circ$, the value for α-abietic acid being −104°, and m. p. 173°.

The author considers that in the change from α-alepic acid to α-abietic acid, an intermediate alepabietic acid is first formed, whereas the β-acid changes directly into α-abietic acid. α-Abietic acid was isolated from the last of the fractional precipitations by water from the alcoholic solution of the pressed gum, which contains about 75% of α- and 25% of β-alepic acid. A. E. C.

Acids contained in the Gum of the Aleppo Pine. II. G. Dupont and L. Desalbres (*Bull. Soc. chim.*, 1924, [iv], **35**, 890—892).—The authors have isolated alepabietic acid (cf. preceding abstract) and shown that β-alepic acid is merely an isomorphous mixture of alepabietic acid and abietic acid. Aleppo pine gum contains α-alepic acid and a certain amount of alepabietic acid and abietic acid. The isomorphism of the two latter acids is proved by crystallographic measurements. A. E. C.

The Phenylalanine Series. V. Hydrogenation of Tyrosine. E. Waser and E. Brauchli (*Helv. Chim. Acta*, 1924, **7**, 740—758; cf. A., 1923, i, 337, 338).—The physical constants and other properties of hexahydrotyrosine already recorded (*loc. cit.*) are incorrect. When tyrosine is catalytically reduced with platinum black, hexahydrophenylalanine is always produced to some extent. Thus, when the hydrogenation is carried out in acid solution, about 75% of the material suffers this change; in neutral suspension, 40—44%; in alkaline suspension very little, *viz.*, only about 16%. Only a little alkali is needed (0·04 equivalent of potassium hydroxide); if one equivalent be present, practically no action takes place. Phenol behaves in a similar way (cf. Willstätter and Hatt, A., 1912, i, 845). Pure hexahydrotyrosine was separated as the ethyl ester. The regenerated l-*hexahydrotyrosine* has m. p. (in a sealed tube, quickly heated) 285° (decomp.), $[\alpha]_D^{20}+14{\cdot}65^\circ$ (in acid solution); its *hydrochloride* has m. p. 238° (decomp.) The *ethyl* ester (which cannot be obtained by hydrogenating tyrosine ester, only hexahydrophenylalanine ester being formed) has m. p. 99—100°, b. p. 184·5°/11 mm., $[\alpha]_D+15{\cdot}19^\circ$; *hydrochloride*, m. p. 261° (decomp.). N-p-*Nitro*-

benzoylhexahydrotyrosine has m. p. 225—226°. 3 : 6-*Di*-p-*hydroxyhexahydrobenzyl*-2 : 5-*diketopiperazine*, which remains behind when the ester is distilled, has m. p. 332° (decomp.). Hexahydrotyrosine yields a *phenylcarbimido* compound, m. p. 112° ($1H_2O$) or 141°, decomp. 145° (anhydrous); when a solution containing this compound and sulphuric acid is evaporated, the *phenylhydantoin* derivative, m. p. 206·5°, is obtained. *l*-Hexahydrophenylalanine, separated from the above, has m. p. 324° (decomp.) or 282° (decomp.), and $[\alpha]_D^{20}+13·30°$; its hydrochloride has m. p. 246°; the chloroplatinate, benzoyl, and other derivatives have already been described (*loc. cit.*) as hexahydrotyrosine chloroplatinate, etc. The *ethyl* ester, obtained as described, either directly or by hydrogenating tyrosine ethyl ester, has b. p. 149—150°/11 mm., $[\alpha]_D^{20}$ $+11·45°$, and forms a *hydrochloride*, m. p. 195—196°. When *d*-phenylalanine is hydrogenated the *l*-isomeride ($[\alpha]_D^{20}+13·32°$) is produced, and the racemic form, also with m. p. 246°, is obtained from *dl*-phenylalanine. When tyramine and *p*-methoxyphenylalanine are catalytically reduced the chief product, in both cases, is *cyclo*hexylethylamine.

Addendum. A New Characteristic Colour Reaction for α-Amino-acids.—When 1 mg. or more of an α-amino-acid (23 compounds gave positive results) is dissolved in 3—4 c.c. of 10% sodium carbonate solution, the solution heated and a few crystals of *p*-nitrobenzoyl chloride are added, a transient but very intense dark red or violet coloration is produced. The reaction is specific for nitrobenzoyl chloride and, as stated, for α-amino-acids, with the exception of glycine and cystine. W. A. S.

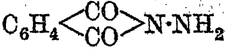
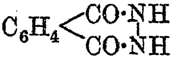
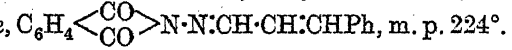
α-Naphthol-4-carboxyarylamides. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 100363, 100364, 100365; from *Chem. Zentr.*, 1924, i, 2011; cf. this vol., i, 173).—The following compounds are described: *α-naphthol*-4-*carboxy*-o-*toluidide*, m. p. 238°; *α-naphthol*-4-*carboxy*-p-*toluidide*, m. p. 215°; *α-naphthol*-4-*carboxy*-N-*methylanilide*, m. p. 232°. G. W. R.

Ketobutyric Acids. FARBWERKE VORM. MEISTER, LUCIUS, U. BRÜNING and F. MAYER (D.R.-P. 376635; from *Chem. Zentr.*, 1924, i, 966—967).—Ketobutyric acids are obtained by the condensation of succinic anhydride with hydrocarbons and their derivatives. Condensation *compounds* (ketobutyric acids) of succinic anhydride with the following compounds are mentioned: with α-naphthyl methyl ether, m. p. 174°; with fluorene, m. p. 109°; with anthracene, m. p. 160°; with diphenylene oxide, m. p. 185°; with acenaphthene, m. p. about 202—203°; with dihydroanthracene, m. p. 156·5—157·5°. G. W. R.

Aromatic Dimethylamines. KALLE UND CO., AKT.-GES. (D.R.-P. 375463; from *Chem. Zentr.*, 1924, i, 966).—Phenyliminodiacetic acid or its derivatives are treated with ferrous sulphate, ferric sulphate, or ferric oxide in acid solution. The following compounds are mentioned: o-*tolyliminodiacetic acid*; *dimethyl*-

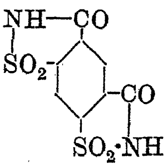
o-*toluidine*; p-*ethoxyphenyliminodiacetic acid*, m. p. 120°; *dimethyl*-p-*phenetidine*. G. W. R.

Melting Point of Acetylsalicylic Acid. M. E. PUTNAM (*Ind. Eng. Chem.*, 1924, **16**, 778).—The melting point of pure acetylsalicylic acid, considered as the temperature of formation of the first liquid globule in a sample contained in a melting-point tube inserted in a bath at 130°, the temperature of which is rising at exactly 3° per minute, is 133·5°. F. G. W.

s-*N*-Aminophthalimide. M. A. MIHĂILESCU and L. FLORESCU (*Bull. Acad. Sci. Roumaine*, 1923, **8**, 303—320; cf. A., 1912, i, 311).—The action of a concentrated aqueous solution of hydrazine sulphate and sodium acetate on a boiling solution of phthalic anhydride in glacial acetic acid yields a product isomeric with those previously obtained by Rottemburg (A., 1894, i, 285) and Försterling (A., 1895, i, 354) to which the constitution  $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N{\cdot}NH_2$ is attributed. s-N-*Aminophthalimide* melts above 340° without subliming. It is sparingly soluble in hot water, hydrolysing slightly to *N*-aminophthalamic acid. The potassium salt, $C_8H_7O_5N_2K$, is identical with that obtained by Försterling from phthalylhydrazide,  $C_6H_4<\genfrac{}{}{0pt}{}{CO{\cdot}NH}{CO{\cdot}NH}$, to which accordingly the structure $C_6H_4(CO_2K)CO{\cdot}NH{\cdot}NH_2$, is now assigned. Only monometallic salts could be obtained and these are precipitated from solution by alcohol, but not by carbon dioxide. They are converted by acids into the original *N*-aminophthalimide. *Diacetyl*-N-*aminophthalimide*, m. p. 132°, by crystallisation from alcohol or boiling water is converted into the *monoacetyl* derivative, $C_{10}H_8O_3N_2$, m. p. 170°. The *monobenzoyl* derivative, m. p. 220—222°, sublimes at 200°. No condensation product could be obtained with acetone or with aliphatic aldehydes or with benzaldehyde. *N*-Aminophthalimide and cinnamaldehyde yield *cinnamylidene*-N-*aminophthalimide*,  $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N{\cdot}N{:}CH{\cdot}CH{:}CHPh$, m. p. 224°. p-*Methoxybenzylidene*-N-*aminophthalimide* has m. p. 188—190°. R. B.

Disaccharins. A. F. HOLLEMAN and H. J. CHOUFOER (*Proc. K. Akad. Wetensch., Amsterdam*, 1924, **27**, 353—360).—The compound of m. p. 129° described by Wischin (A., 1891, 73) as 1 : 3-xylene-2 : 4-disulphochloride on account of its conversion, by heating with phosphorus pentachloride, into 2 : 4-dichloro-*m*-xylene, has been shown to be the dichloride of the 4 : 6-disulphonic acid by synthesis from 6-nitro-*m*-xylene by the following steps: $C_6H_3Me_2NO_2(1:3:6) \longrightarrow C_6H_2Me_2(SO_3H){\cdot}NO_2(1:3:4:6) \longrightarrow C_6H_2Me_2(SO_3H){\cdot}NH_2 \longrightarrow C_6H_2Me_2(SO_3H){\cdot}SH \longrightarrow C_6H_2Me_2(SO_3H)_2(1:3:4:6)$; cf. Pfannenstill (Dissertation, Lund, 1894), and Pollak and Lustig (this vol., i, 30). Some change of orientation must therefore have occurred in Wischin's experiment. This disulphochloride is also the chief product of the action of chlorosulphonic acid on *m*-xylene. It yields a *disulphonamide*, m. p.

249°, which is oxidised by permanganate to the *disaccharin, isophthalicdisulphinide* (annexed formula), m. p. 268—270°, of acid and bitter taste.



The other possible disaccharin derived from *m*-xylene has not yet been prepared, but the oily disulphochloride of a disulphonic acid isolated as a by-product in the sulphonation of *m*-xylene-2-sulphonic acid (Pfannenstill, *loc. cit.*) probably has the required structure, $C_6H_2Me_2(SO_3H)_2(1:3:2:4)$. It yields a *disulphonamide*, m. p. 220°.

Direct sulphonation of *p*-xylene yields the 2 : 6-disulphonic acid, and its disulphonamide does not yield a di-imide on oxidation. *p*-Xylene-2 : 5-disulphonic acid was synthesised from the *p*-xylidinesulphonic acid, $C_6H_2Me_2(NH_2)(SO_3H)(1:4:2:5)$, by replacing the amino group by a sulphonic group. The *disulphochloride*, m. p. 162°, is identical with a by-product observed by Pfannenstill in the action of chlorosulphonic acid on *p*-xylene. It yields a *disulphonamide*, m. p. 310°, oxidised by permanganate to *terephthalic-2 : 5-disulphinide*, m. p. 320°, of bitter taste.

A liquid o-*xylenedisulphochloride* was prepared through the stages: $C_6H_3Me_2(NH_2)(1:2:6) \longrightarrow C_6H_2Me_2(SO_3H)\cdot NH_2(1:2:3:6) \longrightarrow C_6H_2Me_2(SO_3H)\cdot SH \longrightarrow C_6H_2Me_2(SO_3H)_2$, but the orientation of these compounds has not been finally established. The chloride yields a *disulphonamide*, m. p. 251°, converted by permanganate into a *phthalicdisulphinide*, m. p. 275—280°, of bitter taste.

G. M. B.

Ester of Cholic Acid. GEHE U. CO., AKT.-GES., and H. REUME (D.R.-P. 375370 and 381350; from *Chem. Zentr.*, 1924, i, 969).—*Benzyl cholate* is a greyish-white powder, softening at about 69°.

G. W. R.

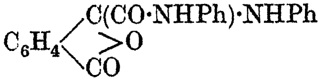
Additive Compounds of Cholic Acid. C. H. BOEHRINGER SOHN, CHEMISCHE FABRIK (D.R.-P. 376470; from *Chem. Zentr.*, 1924, i, 968—969).—The preparation of *additive* compounds of cholic acid with the following aliphatic esters is described: ethyl lactate; amyl acetate; ethyl carbamate; ethyl chloromalonate; bornyl valerate; ethyl butyrate.

G. W. R.

Derivatives of *p*-Aminophenol. KALLE U. CO., AKT.-GES., and E. SPRÖNGERTS (D.R.-P. 383190; from *Chem. Zentr.*, 1924, i, 1592).—The following new compounds are mentioned: p-*ethoxyphenyliminodiacetic acid*, from *p*-phenetidine and chloroacetic acid, m. p. 118° (decomp.); p-*hydroxyphenyliminodiacetic acid*, from *p*-aminophenol and chloroacetic acid, m. p. 165° (decomp.).

G. W. R.

Constitution of Phthalonic Acid. Its Compounds with Aniline. A. CORNILLOT (*Compt. rend.*, 1924, **179**, 274—276; cf. this vol., i, 288, 515).—Evidence for the structure of phthalon-2-anilic acid and phthalondianilide, prepared by Kuroda and Perkin (T., 1923, **123**, 2094), is deduced. The dianilide is stable towards acids and dissolves in concentrated solutions of alkalis and therefore possesses the lactonic structure,



$$C_6H_4\left\langle\begin{matrix}C(CO\cdot NHPh)\cdot NHPh\\ >O\\ CO\end{matrix}\right.$$

It does not react with semicarbazide, but reacts readily as a secondary amine to yield a *phenylurethane*, m. p. 203·5°. The structure is confirmed by its synthesis from aniline and the anilide of α-chlorophthalonic acid. The anilic acid reacts with excess of aniline in benzene solution to yield only the dianilide (the aniline α-anilino-α-hydroxyhomophthalanilate described by Kuroda and Perkin, *loc. cit.*, not being obtained) and therefore behaves as if it possessed the lactonic structure. In alcohol solution, however, a small quantity of an amorphous acid which has the same empirical formula as the dianilide and yields colloidal solutions is obtained. This is the *phenylimine* of phthalon-2-anilic acid,

$$[CO_2H\cdot C_6H_4\cdot C(:NPh)\cdot CONPh]_x,$$

and can only be derived from the ketonic form of the anilic acid. The action of thionyl chloride on the anilic acid yields the anilide of α-chlorophthalonic acid as the main product but in addition a small quantity of the N-*phenylphthalonimide*, m. p. 217°, is produced by dehydration of the ketonic form. The anilic acid thus reacts mainly in its lactonic form but contains a small quantity of the ketonic modification. J. W. B.

α- and β-Disalicylides. R. Anschütz and K. Riepenkröger (*Annalen*, 1924, **439**, 1—8; cf. A., 1920, i, 48).—Salicyloyl chloride heated at 20 mm. begins to lose hydrogen chloride at 110°, decomposition being complete at 180°, and the chloroform solution of the product deposits polysalicylide, whilst the mother-liquor contains the tetrasalicylide. *o*-Diplosal chloride (*o*-salicyloylsalicyloyl chloride) similarly yields a mixture of the poly- and tetra-salicylides. The α-disalicylide is also obtained when diethylaniline is added to an ice-cold solution of salicyloyl chloride in benzene. The product obtained by the action of α-disalicylide on aniline or *p*-toluidine is shown to be the *N*-salicyloyl derivative of the base by the conversion of *o*-diplosalanilide into O-*acetyl*-o-*diplosalanilide*, m. p. 140—141°, which is also obtained by the action of aniline in dry ether on O-*acetyl*-o-*diplosal chloride*, m. p. 104—105°. o-*Diplosalamide* on heating is converted into disalicyloylimide. By excess of ammonia the amide is converted into the ammonium salt of the imide, and by acetyl chloride, in the presence of pyridine, into O-*acetyl*-o-*diplosalamide*, $OAc\cdot C_6H_4\cdot CO_2\cdot C_6H_4\cdot CONH_2$, m. p. 158—159°. *Diacetyldisalicyloylimide*, $(OAc\cdot C_6H_4\cdot CO)_2NH$, has m. p. 114—116°. The β-disalicylide treated with an equimolecular quantity of ammonia in chloroform solution, slowly forms only the yellow ammonium salt of the disalicoylimide, and reacts with aniline only at 155—165°, forming salicoylanilide. J. W. B.

α-Dicresotides. R. Anschütz (*Annalen*, 1924, **439**, 8—19).—By the distillation of the three *O*-acetylcresotic acids under reduced pressure, *o*-, *m*-, and *p*-α-dicresotides corresponding with the disalicylides (cf. preceding abstract) are obtained. No corresponding β-dicresotides were isolated. They are also obtained in good yields by the distillation of the phenyl ester of the respective cresotic acid under 100 mm. Subsequent distillation under 12 mm. yields the dicresotide. By the action of diethylaniline in benzene solution on the *o*-, *m*-, and *p*-cresotoylcresotoyl chlorides (dimethyldiplosal chlorides), hydrogen chloride is split off and the corresponding α-dicresotide produced. Distillation of the α-dicresotide under ordinary pressure yields the corresponding dimethylxanthone. The dicresotides give a series of derivatives corresponding with those of the disalicylides.

[With F. POST and E. CORTY.]—Fractional crystallisation, from chloroform, of the product of distillation of acetyl-*o*-cresotic acid yields also the tetra-*o*-cresotide (α-homosalicylide, A., 1893, i, 166) and by heating under 18 mm. this is practically completely converted into α-dicresotide. *Methyl* o-*cresotoyl*-o-*cresotate* has m. p. 56°. *Di*-o-*cresotoylimide*, $[OH\cdot C_6H_3Me\cdot CO]_2NH$, m. p. 170°, with excess of ammonia yields the *ammonium* salt, from which the corresponding *silver, mercury, copper, calcium, strontium,* and *barium* salts are obtained. It forms an *anilide*, and a p-*toluidide*, m. p. 184°.

[With K. RIEMAR and E. CORTY.]—α-Di-*m*-cresotide is identical with that obtained by Einhorn and Mettler (A., 1903, i, 30). *Phenyl acetyl*-m-*cresotate* has m. p. 71—72°; m-*cresotoylamide*, m. p. 182·5°; m-*cresotoyl*-m-*cresotic acid*, m. p. 162°, *chloride*, m. p. 122°, *methyl* ester, m. p. 115°, *amide*, which on heating yields the *imide*, m. p. 211—212°, forming an *ammonium* salt from which the corresponding *silver, mercury, copper, calcium, strontium,* and *barium* salts are obtained; *anilide*, m. p. 189°, p-*toluidide*, m. p. 202°.

[With R. INDERHEES and A. LÜSSEM.]—α-*Di*-p-*cresotide* has m. p. 197—199°. The *tetra*-p-*cresotide* obtained, by extraction with hot chloroform, from the product of the distillation of acetic acid, acetic anhydride, and *p*-cresotic acid is converted practically completely into the α-di-*p*-cresotide by distillation under 12 mm.; *p*-cresotoyl-*p*-cresotic acid, m. p. 128—129°; *chloride*, m. p. 93—95°; *methyl* ester, m. p. 104—105°; *ethyl* ester, m. p. 97—98°; *acetyl* derivative, m. p. 133—134°; *anilide*, m. p. 159—160°, p-*toluidide*, m. p. 176—177°. The amide on heating yields the *imide*, m. p. 173—174°, of which *ammonium, silver, mercury, copper, calcium, strontium,* and *barium* salts are described. *Diacetyldi*-p-*cresotoylimide* has m. p. 140—141°. J. W. B.

Menthyl αγ-Diacetyl-β-methylglutarate. H. RUPE and F. BECHERER (*Helv. Chim. Acta*, 1924, 7, 670—681).—The following results were obtained in an abortive effort to prepare an alcohol possessing high optical activity. Menthyl acetoacetate (A., 1913, i, 884) and acetaldehyde undergo the Knoevenagel condensation and yield two isomeric forms of *menthyl αγ-diacetyl-β-methylglutarate*. The chief product has m. p. 200° and $[\alpha]_D^{20}$ −49·01°, and affords a *semicarbazone*, m. p. 196—197°; the subsidiary product, not isolated in every case, has m. p. 152° and $[\alpha]_D^{20}$ −26·48°, its *semicarbazone* melting at 165—166°. The second form is converted into the first by recrystallisation from benzene, the product having, however, $[\alpha]_D^{20}$ −68·01°. When ethyl αγ-diacetyl-β-methylglutarate is heated with one molecular proportion of menthol at 150—160°, *menthyl ethyl αγ-diacetyl-β-methylglutarate*, m. p. 154—155°, $[\alpha]_D^{20}$ −28·99°, is obtained (*semicarbazone*, m. p. 169—170°); this, heated with more menthol, affords the second form, m. p. 152—153°, of the ester described above. The ester of m. p. 200° is converted by treatment in ethereal solution with a little hydrogen chloride into *menthyl 5-keto-*1 : 3-*dimethyl*-Δ^6-cyclo*hexene*-2 : 4-*dicarboxylate*, m. p. 185—186°, $[\alpha]_D^{20}$ −27·90°, *semicarbazone*, m. p. 179—180°, whilst the ester of m. p. 152°, similarly treated, yields a stereoisomeric form of this cyclic compound, m. p. 137—138°, $[\alpha]_D^{20}$ −56·27°, *semicarbazone*, m. p. 104—105°. The isomerism of the above compounds is discussed, it being pointed out that all three carbon atoms in the glutaric acid " spinal column " are asymmetric. Reduction of the menthyl ethyl αγ-diacetyl-β-methylglutarate by Bouveault and Blanc's method failed to give a primary alcohol and hydrolysis of the dimenthyl ester did not take place normally. W. A. S.

Attempts to Synthesise Benzophenone-2 : 3′ : 4′-tricarboxylic Acid. H. DE DIESBACH and P. BULLIARD (*Helv. Chim. Acta*, 1924, **7**, 618—627).—Benzophenone-2 : 3′ : 4′-tricarboxylic acid, Limpricht's " phthaloylphthalic acid," can easily be produced from *o*-xylene, but pure supplies of the latter are not readily obtainable. The preparation of the compound by other methods has therefore been investigated. 3′-Amino-4′-methylbenzophenone-2-carboxylic acid (Limpricht, A., 1898, i, 322) is converted by the Sandmeyer reaction into *3′-cyano-4′-methylbenzophenone-2-carboxylic acid*, m. p. 194°, of which the *methyl* ester, m. p. 87·5°, and the *copper* salt are described. This nitrile is not hydrolysed by sulphuric acid without condensation to anthraquinone derivatives also taking place, but boiling 30% potassium hydroxide converts it into the expected 4′-*methylbenzophenone*-2 : 3′-*dicarboxylic acid*, m. p. 216°; *dimethyl* ester, m. p. 94°. Treatment of the nitrile with nitric acid, *d* 1·15 at 200° for 8 hours, brings about simultaneous oxidation and hydrolysis, " phthaloylphthalic acid " being obtained. The product has m. p. 199·5°, higher than any previously recorded.

The conversion of 2 : 3′-dichloro- or -dibromo-4′-methylbenzophenone into the corresponding 2 : 3′-dicarboxylic acid by treatment with cuprous cyanide and pyridine (cf. de Diesbach, A., 1923, i, 804, etc.) was examined as an alternative. The results of the unsuccessful experiments illustrate the conditions under which the replacement of halogen by the cyano group takes place. *o*-Bromobenzophenone, when simply boiled with pyridine and cuprous cyanide for two days, affords o-*benzoylbenzonitrile*, m. p. 83·5°, b. p. 215—225°/20 mm., yielding anthraquinone when treated with sulphuric acid and *o*-benzoylbenzoic acid when submitted to the action of nitric acid, *d* 1·15, at 150°. 3-Chloro-4-methylbenzophenone (Heller, A., 1913, i, 631) is not attacked by cuprous cyanide and pyridine even at 200°. When a mixture of benzoyl chloride and *o*-bromotoluene is treated with aluminium chloride a product is obtained which is stated by Mayer and Freund (A., 1922, i, 865) to be a mixture of 3- and 2-bromo-4-methylbenzophenones. Actually the substance, an oil of b. p. 195—210°/24 mm., interacts with cuprous cyanide and pyridine at 150° to yield an oil from which a small quantity of 3-*cyano*-4-*methylbenzophenone*, m. p. 106·5°, convertible into 4-benzoylphthalic acid, is obtained, yet if the crude nitrile be simultaneously oxidised and hydrolysed, and the impure dicarboxylic acid obtained purified by fractional crystallisation of its copper salt, the product is benzophenone-2 : 4-dicarboxylic acid. Thus migration of the bromine atom during the reaction with aluminium chloride, as described by Mayer and Freund, has taken place. When *o*-chlorobenzoyl chloride and *o*-chlorotoluene are treated with aluminium chloride in suspension in carbon disulphide, 2 : 3′-*dichloro*-4′-*methylbenzophenone*, m. p. 43·5°, b. p. 220—221°/24 mm., is obtained; the corresponding 3′-*chloro*-2-*bromo*-4′-*methylbenzophenone*, prisms, m. p. 50°, b. p. 229—231°/25 mm., is produced from *o*-bromobenzoyl chloride. When the first of these is treated with cuprous cyanide in pyridine at 200°, or the second at the b. p. of pyridine, 3′-*chloro*-2-*cyano*-4′-*methylbenzophenone*, m. p. 118·5°, is produced, yielding 3-chloro-4-methylbenzophenone-2′-carboxylic acid on hydrolysis. If the reaction with cuprous cyanide in pyridine be carried out at higher temperatures, complex products, still containing chlorine, are obtained; the chlorine atom therefore is not labile. *o*-Bromobenzoyl chloride and *o*-bromotoluene give a mixture of 2 : 3′- and 2 : 2′-*dibromo*-4′-*methylbenzophenones*, an oil, b. p. 240—243°/24 mm., solidifying eventually and then melting at 51°. When it is treated for two days with cuprous chloride and pyridine at 150° a mixture is obtained from which, if the pyridine be removed by distillation, a small amount of a *dinitrile*, m. p. 110°, can be separated; if however, the pyridine be removed by treating the mixture with hydrochloric acid, another product, possibly an *amide*, m. p. above 250°, is obtained. Both yield "phthaloylphthalic" acid when treated with dilute nitric acid at 200°. A further attempt to prepare phthaloylphthalic acid was based on the replacement, as above, of the chlorine atom in 3′-chloro-4′-methylbenzophenone-2-carboxylic acid, obtained from phthalic anhydride and *o*-chlorotoluene. Actually the chlorine atom remained in its place, but the carboxyl radical was detached, the product of the action of the cuprous cyanide and pyridine at 200° being 3-chloro-4-methylbenzophenone: substitution by the "phthaloyl" radical takes place therefore in the *para*-position to the methyl group, not to the chlorine atom as stated by Heller (*loc. cit.*). W. A. S.

Products of Decomposition of Benzaldoxime Peroxide. E. Parisi (*Gazzetta*, 1924, 54, 485—490; cf. A., 1923, i, 579; this vol., i, 52).—When kept between filter-paper, benzaldoxime peroxide undergoes gradual decomposition, yielding α-benzaldoxime, benzaldehyde, benzoic acid, benzonitrile, dibenzenylazoxime, and the

N-benzoyl derivative of benzhydroxamic acid. A cold 10% solution of potassium hydroxide in alcohol also decomposes the peroxide, with formation of nitrogen, ammonia, nitrous acid, β-benzaldoxime, benzoic acid, hydroxamic acid, and dibenzenylazoxime.

T. H. P.

Colour and Molecular Geometry. II. Explanation of the Results of Chattaway and Clemo. J. Moir (*J. Chem. Soc.*, 1924, **125**, 1548—1551; cf. *ibid.*, 1923, **123**, 3041).—Alternate single and double bonds do not *per se* imply the possession by the substance of a "high" colour and the experimental results of Chattaway and Clemo are considered to be better accounted for by the orbit theory than by Hewitt's theory. In *p*-nitrobenzaldehyde phenylhydrazone, the orbit of the revolving electron surrounds the chain $NO_2\cdot C_6H_4\cdot CH{:}N\cdot N$. When CH_2 is substituted for the secondary amino group, the orbit contracts to include only the chain $NO_2\cdot C_6H_4\cdot CH{:}N$. Hence the wave-length of the characteristic absorption band is decreased and the substance exhibits a lower colour. In *p*-nitrophenylhydrazine and benzylidene-*p*-nitrobenzylamine, the orbit is assumed to surround the chains $NO_2\cdot C_6H_4\cdot N{:}N$ and $NO_2\cdot C_6H_4\cdot CH{:}N$, respectively. Hence the absorption bands of these substances should be, as in fact they are, in nearly the same position. With benzaldehyde-*p*-nitrophenylhydrazone the interfocal distance of the orbit is supposed to be the same as in *p*-nitrophenylhydrazine, but since the orbit now embraces the bulky benzylidene group, the periodic time of the electron is greater and hence the colour of the substance is higher. In general, the wave-length absorbed increases with the magnitude of the "loading." Results of the spectroscopic examination of some of the substances in the presence and absence of potassium hydroxide are given.

W. E. E.

Isomerism of the Oximes. XIX. Substituted Cinnamaldoximes. O. L. Brady and H. J. Grayson (*J. Chem. Soc.*, 1924, **125**, 1418—1421; cf. *ibid.*, 1922, **121**, 2098).—o-*Methoxycinnam*anti*aldoxime*, prepared by the action of hydroxylamine hydrochloride on the aldehyde suspended in sodium hydroxide solution, has m. p. 82°. The *acetyl* derivative also has m. p. 82°. It dissolves slowly in warm 2*N*-sodium hydroxide giving the sodium salt of the original oxime, thus establishing the *anti*-configuration of the latter. Thus *o*-methoxy- resembles the nitro-cinnamaldehydes, rather than the cinnamaldehydes. o-*Methoxycinnam*syn*aldoxime*, m. p. 135·5°, is obtained in the absence of alkali; *hydrochloride*, m. p. 142° (decomp.). The *acetyl* derivative, m. p. 77°, is formed instead of the usual nitrile by the action of acetic anhydride at 30°. *Benzoyl*-o-*methoxycinnam*anti*aldoxime*, m. p. 128°, is obtained from both the *syn*- and *anti*-oximes; it yielded only the *anti*aldoxime on hydrolysis (cf. T., 1922, **121**, 2098). The 2 : 4-*dinitrophenyl ether* of *o*-methoxycinnam*syn*aldoxime, m. p. 202° (decomp.), is obtained from the *anti*-oxime. m-*Nitrocinnam*syn*aldoxime*, m. p. 163°, was obtained when the *hydrochloride*, m. p. 175° (decomp.)

(formed on saturating a solution of the *anti*-oxime in hot benzene with hydrogen chloride), was treated with sodium hydroxide. Admixture with the *anti*-isomeride (m. p. 157°) caused a depression of the m. p.; its *acetyl* derivative, m. p. 98—100°, yielded *m*-nitrocinnamonitrile with alcoholic potassium hydroxide; this fixes its entity, as the *anti*-oxime under similar conditions gives an *acetyl* compound (m. p. 136°) from which the *anti*-oxime is regenerated. o-*Nitrocinnam*syn*aldoxime*, m. p. 138°, was obtained through its *hydrochloride*, m. p. 144° (decomp.), similarly to the *m*-nitro-compound. A purer compound, m. p. 140°, was obtained by Dunstan and Thole's method (P., 1911, **27**, 233). Its conversion into *o*-nitrocinnamonitrile proved its *syn*-configuration. p-*Nitrocinnam*syn*aldoxime* was not obtained in the pure state; its *hydrochloride*, m. p. 173° (decomp.), gave an oxime of m. p. 140° which depressed the m. p. (179°) of the *anti*-isomeride. A. C.

Preparation of Piperonal from *iso*Safrole and α-Homopiperonal from Safrole by Ozone. S. Nagai (*J. Fac. Eng. Tokyo*, 1923, **13**, 185—192).—*iso*Safrole ozonide is readily prepared by passing ozonised air into a solution of *iso*safrole in perfectly dried solvents, *e.g.*, a mixture of chloroform, carbon tetrachloride or tetrachloroethane, and light petroleum. The ozonide decomposes spontaneously at the ordinary temperature, more readily on heating gently or in presence of water, with the production of considerable amounts of resinous matter. The best yield of piperonal is obtained when the ozonide is decomposed in the presence of reducing agents; thus, by employing a saturated aqueous solution of sodium hydrogen sulphite a yield of 85% of theory was produced.

Safrole ozonide is obtained in a similar manner, but owing to its lesser solubility mixed solvents are not required. The best method of decomposition of the ozonide consists in the gradual addition of zinc dust and water to its solution in glacial acetic acid, when yields of 60—65% of α-homopiperonal result. The aldehyde has b. p. 131—133°/8 mm., d_4^{15} 1·2654, n_D^{15} 1·5547; *oxime*, m. p. 109°, *semicarbazone*, m. p. 175—176°, and *phenylhydrazone*, m. p. 176°. C. J. S.

Photochemical Reactions in Solutions of the Alkali Halides in Acetophenone. J. L. R. Morgan, O. M. Lammert, and R. H. Crist (*J. Amer. Chem. Soc.*, 1924, **46**, 1170—1178).—Pure acetophenone is decomposed by the light from a quartz-mercury lamp, apparently with the production of benzoic acid. A yellow colour appears, possibly due to the formation of condensation products, and the specific electrical resistance decreases. In the dark this again increases, but the yellow colour continues to deepen. The presence of water accelerates the reaction. A solution of sodium iodide in acetophenone increases in resistance in the light, iodine is liberated, and a fine, white deposit, which appears to be sodium benzoate, is formed. There are breaks in the curves showing variation of resistance with time, thus indicating that concurrent or overlapping reactions are taking place in the solution. A scheme of combined thermal and photochemical reactions has therefore been put forward as a possible explanation of the changes observed.

The effective wave-lengths for the reactions in glass vessels are 300 $\mu\mu$ and 400 $\mu\mu$. The effects are more pronounced and differ somewhat in character in quartz vessels, indicating that the shorter wave-lengths are more effective for at least some of the reactions.

M. S. B.

Beckmann's Rearrangement. XII. Catalytic Action of Reduced Copper on Acetophenoneoxime. S. YAMAGUCHI (*Mem. Coll. Sci. Kyoto*, 1924, **7**, 281—285).—Acetophenoneoxime, when passed with hydrogen over reduced copper at 200°, yielded benzoic acid, ammonium benzoate, α-phenylethylamine, αα-diphenylethylamine, benzonitrile, acetophenone, and unchanged oxime.

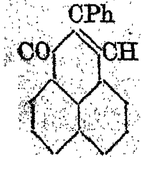
F. G. M.

Mono- and Di-chloro-1-ketotetrahydronaphthalene. TETRALIN G.M.B.H. and W. RIEBENSAHM (D.R.-P. 377587; from *Chem. Zentr.*, 1924, i, 956).—By chlorination of 1-ketotetrahydronaphthalene are obtained *dichloro*-1-*ketotetrahydronaphthalene*, m. p. 75—76°, and *monochloro*-1-*ketotetrahydronaphthalene*, m. p. 45°. G. W. R.

Changes in State of Aggregation and Polymorphism. IV. Formation of Metastable Benzophenone. K. SCHAUM and K. ROSENBERGER (*Z. anorg. Chem.*, 1924, **136**, 329—336).—The addition of hydrogen chloride to either the rhombic α or the monoclinic, metastable, β form of benzophenone results in an equilibrium being established between the two modifications, which, at low temperatures, corresponds with the formation of the eutectic mixture. The hydrogen chloride acts as a catalyst in this change probably by forming an unstable additive product with the benzophenone since, on passing the gas into the molten compound, the latter develops a bright grass-green colour. This view is strengthened by the fact that compounds, such as metallic chlorides, which are known to give additive products with benzophenone also accelerate the change from the stable α to the metastable β form. Benzophenone forms eutectic mixtures with 70 and 30 mol.% of diphenylamine (m. p. 29·5° and 25° respectively), with 39 mol.% of benzhydrol (m. p. 23°), with 24 mol.% of triphenylmethane (m. p. 33°), with 10 mol.% of 4 : 4′-dichlorobenzophenone (m. p. 43°), and with 26 mol.% of ditolyl ketone (m. p. 34°). Of a number of substituted benzophenones tested only *p*-ditolyl ketone exhibited polymorphism.

A. R. P.

Vat Dyes. KALLE U. Co. (D.R.-P. 384982; from *Chem. Zentr.*, 1924, i, 1111).—*Potassium* 1-*aldehydonaphthalene*-8-*carboxylate* condenses with phenylacetonitrile to give 1-β-*cyanostyrylnaphthalene*-8-*carboxylic acid*, m. p. 162—165°, which is converted by sulphuric acid into 2-*phenylperinaphthindone* (annexed formula), m. p. 142°. The last is converted by fusion with potassium hydroxide into a blue vat dye. G. W. R.



Aryl 4-Hydroxynaphthyl Ketones. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 100366, 100367, 100368, 100369, 100370, and 100371; from *Chem. Zentr.*, 1924, i, 2204—2205; cf. this vol., i, 174—175).—The following new compounds are mentioned: o-*chlorophenyl* 4-*hydroxynaphthyl ketone*, m. p. 216°; p-*chlorophenyl* 4-*hydroxynaphthyl ketone*, m. p. 210°; 2 : 4-*dichlorophenyl* 4-*hydroxynaphthyl ketone*, m. p. 222°. G. W. R.

An Aryl Hydroxynaphthyl Ketone. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 101402; from *Chem. Zentr.*, 1924, i, 2205; cf. preceding abstract).—2-*Benzoyl*-1-*naphthol*-4-*sulphonic acid* is obtained by the action of benzotrichloride on sodium 1-naphthol-4-sulphonate. G. W. R.

Residual Affinity and Co-ordination. XVIII. Interaction of Zirconium Salts and β-Diketones. G. T. MORGAN and A. R. BOWEN (*J. Chem. Soc.*, 1924, **125**, 1252—1261).—The method developed by Biltz and Clinch (A., 1904, i, 715) to form zirconium acetylacetone in aqueous solution proved impracticable when tried with homologues of acetylacetone, whilst the higher aliphatic diketones and sodium benzoylacetone (which produced zirconyl bisbenzoylacetone) also gave unsuccessful results. In place of this, a general reaction was obtained between anhydrous zirconium tetrachloride and the β-diketones in dry chloroform or benzene, whereby three chlorine atoms were replaced. *Zirconium trisdibenzoylmethane chloride*, so obtained, is very stable in the dry state and gives crystalline double salts such as the *ferrichloride*, *chloroaurate*, and *chloroplatinate*. *Zirconium trisbenzoylacetone chloride* is less stable, whilst the *trisacetylacetone chloride* is the most readily hydrolysable member of the series. A. COUSEN.

Action of Selenium Tetrachloride on Di- and Tri-ketones. Selenium Phenylacetyl- and β-Phenylpropionyl-acetones. G. T. MORGAN and C. R. PORTER (*J. Chem. Soc.*, 1924, **125**, 1269—1277).—The copper derivative of ω-phenylacetylacetone reacts readily with selenium tetrachloride producing mainly the dimeric *selenium* ω-*phenylacetylacetone* and 3-*chloro*-ω-*phenylacetylacetone*. β-Phenylpropionylacetone similarly reacts to give *selenium* β-*phenylpropionylacetone*. These compounds, reduced with hydriodic acid, give *diselenium bis*-ω-*phenylacetylacetone* and *bis*-β-*phenylpropionylacetone*, respectively, anhydrous hydrocyanic acid also reacting to give *cyanoselenium* ω-*phenylacetylacetone* and the β-phenylacetylacetone. The products are all enolic, the reduction compounds being orange-coloured oils which are also obtained as by-products of the original condensations. Selenium tetrachloride reacts with the barium salt of diacetylacetone chiefly as a dehydrating and chlorinating agent, the chief derivative being 3 : 5-*dichloro*-2 : 6-*dimethylpyrone*, white needles, m. p. 148—150°, whilst much free selenium is also obtained. This pyrone with barium hydroxide affords an enolic substance, probably 3-*chloro*-5-*acetyl*-4-*hydroxy*-2-*methylfuran*, m. p. 83—84°. Chlorination of barium diacetylacetone yields *trichlorodiacetylacetone*,

$$COMe{\cdot}CCl_2{\cdot}CO{\cdot}CHCl{\cdot}COMe,$$

m. p. 105—106°. A. COUSEN.

1-Chloro-2-acylamidoanthraquinones. E. Kopetschni (D.R.-P. 376471; from *Chem. Zentr.*, 1924, i, 967).—β-Acylamidoanthraquinones are chlorinated by means of sulphuryl chloride in an indifferent solvent. 1-*Chloro-2-acetamidoanthraquinone* has m. p. 241°; 1-*chloro*-2-p-*toluenesulphamidoanthraquinone*, green needles, m. p. 204—205° (decomp.); *sodium* salt of the latter,

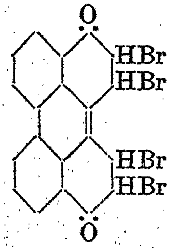
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_2Cl(NNa\cdot SO_2\cdot C_7H_7),$$

red crystals. G. W. R.

Sodium Alizarate and Alumina. F. S. Williamson (*J. Phys. Chem.*, 1924, **28**, 891—892).—Experiments are described from which the author infers that no definite aluminium alizarate is formed when aluminium hydroxide and sodium alizarate are mixed, contrary to the supposition of Liechti (*J. Soc. Chem. Ind.*, 1886, **5**, 523). S. B.

Action of Thionyl Chloride on Hydroxyanthraquinones. I. Thionylalizarin. A. Green (*J. Chem. Soc.*, 1924, **125**, 1450—1451).—*Thionylalizarin*, $C_{14}H_6O_2{<}\genfrac{}{}{0pt}{}{O}{O}{>}SO$, prepared by the action of boiling thionyl chloride on dry alizarin, forms yellow crystals, m. p. 171—172°; the colour changes to orange-yellow after a few hours in a sealed tube, but the m. p. and sulphur content remain unchanged. The substance is stable in dry air, but converted into alizarin by moisture. The colours of its solutions in aqueous sodium hydroxide and concentrated sulphuric acid are the same as those of alizarin. *Alizarin monoacetate*, m. p. 201—202°, is formed on boiling thionylalizarin with glacial acetic acid, and the *diacetate*, m. p. 185°, on using acetic anhydride. A. C.

Perylene and its Derivatives. IV. A. Zinke and H. Schöpfer [with G. Müller, R. Sabathy, M. Schneider, and W. Spitzy] (*Monatsh.*, 1924, **44**, 365—370).—Careful bromination of perylenequinone in the cold yields, besides dibromoperylenequinone (A., 1920, i, 541), 1 : 2 : 11 : 12-*tetrabromotetrahydroperylenequinone* (annexed formula), bright yellow needles, rapidly darkening, which readily loses hydrogen bromide, giving dibromoperylenequinone. On chlorination in nitrobenzene on the water-bath, perylenequinone similarly yields 1 : 2 : 11 : 12-*tetrachlorotetrahydroperylenequinone*, which is more stable than the tetrabromo compound, but at about 265°, or by crystallisation from aniline or heating with pyridine, is converted into *dichloroperylenequinone*, which dyes cotton pure yellow. Nitration of perylenequinone with concentrated nitric acid in boiling acetic acid solution gives, besides the mononitro derivative previously described (Zinke and Unterkreuter, *loc. cit.*), a *dinitroperylenequinone*, $C_{20}H_8O_2(NO_2)_2$, which dyes cotton dull violet. On reduction with alkaline sodium hyposulphite, the mononitro compound yields *aminoperylenequinone*, $C_{20}H_9O_2\cdot NH_2$,



and the dinitro compound gives diaminoperylenequinone, $C_{20}H_{12}O_2N_2$; *diacetyl* derivative; *dibenzoyl* derivative, needles.

R. B.

Perylene and its Derivatives. V. A. ZINKE and A. PONGRATZ (*Monatsh.*, 1924, **44**, 379—382).—Perylenequinone stands between α-naphthaquinone and anthraquinone in its quinonoid properties, and is much more stable than *pp'*-diphenoquinone, from which it is genetically derived (cf. Willstätter and Kalb, A., 1905, i, 361). It gives no reaction with aqueous hydriodic acid in nitrobenzene solution or with guaiacum resin or hæmatoxylin in alcoholic solution. With phenylhydrazine and hydroxylamine at higher temperatures, it yields no hydrazone or oxime, but apparently undergoes reduction. It does not react with sulphurous acid, but is reduced by stannous chloride in acetic acid solution. A solution of perylenequinone in acetic acid, on the addition of potassium iodide, gives after some minutes a reaction for free iodine; *p*-benzoquinone gives an immediate reaction, α-naphthaquinone after a few seconds, and anthraquinone an uncertain reaction after 30 to 35 mins. The solution of perylenequinone gradually deposits brownish-violet needles of *perylenequinhydrone*, $C_{40}H_{20}O_4$. *Perylenequinol*, $C_{20}H_{12}O_2$ (cf. Zinke and Unterkreuter, A., 1920, i, 541), obtained by reduction of perylenequinone with potassium iodide and red phosphorus in acetic acid solution, or with zinc dust and acetic acid, shows an intense yellowish-green fluorescence in solution and readily oxidises in air to a quinhydrone.

R. B.

Aminoperylenequinones. H. PEREIRA (Brit. Pat. 199721).—Mononitro-, dinitro-, and *bromodinitro*-perylenequinones afford, on reduction with hot alkaline sodium hyposulphite, *monoamino-*, *diamino-*, and *bromodiamino-perylenequinones*, respectively, all of which form dark needles and dye cotton in brown to violet shades (cf. A., 1920, i, 542, and Brit. Pat. 199720). F. G. W.

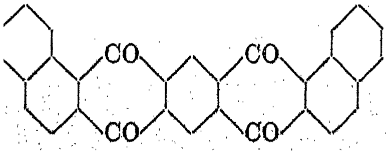
Attempt to Synthesise Dinaphthanthracenediquinone [Dinaphthanthradiquinone]. H. DE DIESBACH and L. CHARDONNENS (*Helv. Chim. Acta*, 1924, **7**, 609—613).—When "phthaloylphthalic anhydride" (the anhydride of benzophenone-2 : 3' : 4'-tricarboxylic acid; Limpricht, A., 1900, i, 599) and benzene are treated with aluminium chloride, 1 : *5-dibenzoylbenzene-2 : 2'-dicarboxylic acid*, m. p. 177—180°, is produced. This undergoes further condensation when treated with strong sulphuric acid on the water-bath, yielding *2-benzoylanthraquinone-2'-carboxylic acid*,

$$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_{14}H_7O_2,$$

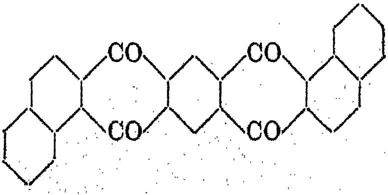
yellow prisms giving a bottle-green "vat" with sodium hydrosulphite, soluble in benzene, m. p. 218° after sintering at 198°, together with a little 2-benzoylanthraquinone-3-carboxylic acid, insoluble in benzene and giving a reddish-brown "vat" (cf. Fairbourne, T., 1921, **119**, 1580). The former was also prepared by condensing phthalic anhydride with 9 : 10-dihydroanthracene, much anthroylbenzoic acid or similar compounds being formed as by-products (cf. Schaarschmidt, A., 1916, i, 381); further condensation to dinaphthanthradiquinone was not satisfactorily brought about. 1-*p*-Methylbenzoyl-5-benzoylbenzene-2 : 2′-dicarboxylic acid undergoes a similar condensation, not wholly decomposition, as stated by Limpricht (*loc. cit.*), when heated with strong sulphuric acid, yielding 2 : 6-*benzoylmethylanthraquinone-2′-carboxylic acid*, m. p. 213°. (Cf. this vol., i, 1074.) W. A. S.

Dibenzoylxylenes and Dinaphthanthradiquinones. II. H. DE DIESBACH and L. CHARDONNENS (*Helv. Chim. Acta*, 1924, 7, 614—618; cf. A., 1923, i, 804).—When α-cumidic acid is treated with sulphuric acid and potassium nitrate at 50° it yields solely a mononitro derivative, 2-*nitro*-m-*xylene*-4 : 6-*dicarboxylic acid*, m. p. 294°, the *dimethyl* ester of which has m. p. 143·5—144·5°. Reduction of the nitro-acid affords the corresponding *amino-acid*, m. p. 305—306°, the *dimethyl* ester of which has m. p. 95·5—97°. By the action of phosphorus pentachloride followed by aluminium chloride, on a solution of the nitrocumidic acid in benzene 2-*nitro*-4 : 6-*dibenzoyl*-m-*xylene* is obtained, m. p. 126—127°. This compound is oxidised by the action of nitric acid, *d* 1·15, at 200°, affording 2-*nitro*-4 : 6-*dibenzoyl*iso*phthalic acid*, m. p. 235—238°, which, by treatment with sulphuric acid at 200°, is converted into 6-*nitro*-5 : 7 : 12 : 14-*dinaphthanthradiquinone*, subliming without melting at 285—290°. W. A. S.

Some Derivatives of Dinaphthanthradiquinone and the Synthesis of Dinaphthalinoanthradiquinone. H. DE DIESBACH and V. SCHMIDT (*Helv. Chim. Acta*, 1924, 7, 644—653; cf. A., 1923, i, 804; Philippi, A., 1923, i, 576; 1913, i, 627).—Pyromellitic anhydride and toluene react (Philippi, *loc. cit.*) in presence of aluminium chloride to give a mixture of much 4 : 6-di-*p*-toluoyl*iso*phthalic acid, the *methyl* ester of which has m. p. 194—195°, and a little 2 : 5-di-*p*-toluoylterephthalic acid, *methyl* ester, m. p. 203°, less soluble in alcohol than its isomeride. Philippi's conclusions (*loc. cit.*) as to the possibility of further condensation taking place are now shown to be unfounded; when the crude mixture of the above acids, or the first alone, is treated with 90% sulphuric acid at 180°, a poor yield of 2 : 10-*dimethyl*-5 : 7 : 12 : 14-*dinaphthanthradiquinone* is obtained, not melting below 350°, which, like its congeners described previously and below, yields a brown "hyposulphite vat" which turns blue on exposure to air. The isomeric 2 : 9-*dimethyl*-5 : 7 : 12 : 14-*dinaphthanthradiquinone* was also obtained. Similarly, pyromellitic anhydride and *o*-chlorotoluene yield (82% of theory) 4 : 6-*di-3′-chloro*-p-*toluoyl*iso*phthalic acid*, m. p. 302°, which affords a *methyl* ester, m. p. 234—235°, and 2 : 5-*di*-3′-*chloro*-p-*toluoylterephthalic acid*, m. p. 315°, *methyl* ester, m. p. 241°. When the crude mixture of acids is heated with 90% sulphuric acid at 180°, 40% of the theoretical yield of the corresponding dinaphthanthradiquinones is obtained. The two substances are separated by fractional extraction with nitrobenzene. Neither interacts with toluidine in presence of sodium acetate and a copper salt; the chlorine atoms therefore are not adjacent to the carbonyl groups. 3 : 9-*Dichloro*-2 : 10-*dimethyl*-5 : 7 : 12 : 14-*dinaphthanthradiquinone* decomposes at 320°, whilst 3 : 10-*dichloro*-2 : 9-*dimethyl*-5 : 7 : 12 : 14-*dinaphthanthradiquinone* remains unmelted at 350°. From *p*-chlorotoluene, in like manner, 4 : 6-*di*-3′-*chloro*-o-*toluoyl*iso*phthalic acid*, m. p. 313°, giving a *methyl* ester, m. p. 164—165°, was obtained, together with 2 : 5-*di*-3′-*chloro*-o-*toluoylterephthalic acid*, m. p. 325°, *methyl* ester, m. p. 182°. The first of these, or the crude mixture, as it contains only a very small proportion of the second acid, yields 4 : 8-*dichloro*-1 : 11-*dimethyl*-5 : 7 : 12 : 14-*dinaphthanthradiquinone*, m. p. 270° (decomp.). When aluminium chloride is added to a solution of pyromellitic anhydride, naphthalene, and benzene at 30°, and the mixture heated during 10 hours at 30—60°, two acids are obtained which may be separated from one another by fractional crystallisation from water, acetic acid, and alcohol, used in succession. 4 : 6-*Di*-α-*naphthoyl*iso*phthalic acid* has m. p. (when anhydrous) 302°; its *methyl* ester has m. p. 205°. 2 : 5-*Di*-α-*naphthoylterephthalic acid* has m. p. 316°. For effecting the further condensation to the anthradiquinone derivatives, sulphuric acid cannot be used, because sulphonation takes place (some products of the action are described); but the reaction can be brought about by heating the acid with phosphorus pentoxide at 300—310°. If the crude mixture of acids be used, a product is obtained which may be separated into its two components by fractional extraction with acetic acid and crystallisation from nitrobenzene; or the two isomerides may be prepared each from its appropriate acid. In this way 1 : 2 : 10 : 11-*dibenzo*-5 : 7 : 12 : 14-*dinaphthanthradiquinone* (syn-biangular-2 : 3 : 6 : 7-*dinaphthalino*-1 : 4 : 5 : 8-*anthradiquinone*, Stelzner's nomenclature), brick-red needles, decomposing without melting at 320° (I), and the corresponding 1 : 2 : 8 : 9-compound (anti-biangular-2 : 3 : 6 : 7-*dinaphthalino*-1 : 4 : 5 : 8-*anthradiquinone*), somewhat paler needles,



(I.)



(II.)

unaltered even at 360° (II), are obtained. Both substances yield a violet "vat" with sodium hyposulphite, the colour changing to green and eventually to orange, on exposure to air.

When tetrahydronaphthalene is used instead of naphthalene, the condensation takes place smoothly and appears to result in the production of only one of the possible isomerides, *viz.*, 4 : 6-*di*-β-ar-*tetrahydronaphthoyl*iso*phthalic acid*, m. p. 289—290°. Attempts to convert this compound into an anthradiquinone failed, oxidation taking place at high temperatures. W. A. S.

Action of Tetrachloro- and Tetrabromo-phthalic Acids on Turpentines. New Method of Preparing Camphols and *d*- and *l*-Camphor. A. HALLER (*Compt. rend.*, 1924, **178**, 1933—1937; cf. Bouchardat and Lafont, A., 1892, 199; Bouchardat and Tardy, A., 1895, i, 673).—Bornyl and fenchyl esters may be prepared by the action of acids on terpenes provided that the acid used is soluble in the terpene. Tetrahalogenophthalic acids fulfil this condition and react with pinenes yielding bornyl, *iso*bornyl, and fenchyl esters from which mixtures of these alcohols may be obtained on hydrolysis. Both the yield and the relative proportion of esters obtained depend on the temperature and also on the duration of the reaction, and details of experiments carried out with turpentine from *Pinus maritima* and *P. halepensis* and tetrachloro- and tetrabromo-phthalic acids under different conditions are given.

H. J. E.

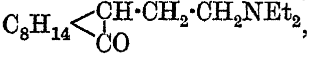
The Camphor and Camphenilone Series. Reply to L. Ruzicka. S. NAMETKIN (*Annalen*, 1924, **438**, 202).—Explanatory (cf. this vol., i, 64).

W. A. S.

The Camphenilane Series. S. NAMETKIN (*Annalen*, 1924, **438**, 185—201).—A review of earlier work (cf. A., 1915, i, 699) with particular reference to the results of Komppa and Roschier (A., 1922, i, 1167). The compound described as β-nitrocamphenilane (Nametkin and Chuchrikova, A., 1915, i, 701) is now termed α-nitrocamphenilane, whilst the 6-nitro- is now the 2-nitro derivative. The *apo*fenchocamphoric acid previously described (m. p. 144·5—145°) is now shown to be cis-apo*fenchocamphoric acid.* Various salts are briefly described. The solubility of the acid in water is 0·72 g. per 100 c.c. at 19°. With acetyl chloride in the cold, it yields the *anhydride*, m. p. 136—137°. The acid affords a *monoanilide*, m. p. 155—157°, and a *dianilide*, m. p. 148—150°. trans-apo*Fenchocamphoric acid*, m. p. 147—148°, is obtained when the *cis*-variety is heated with hydrochloric and acetic acids at 180—200°. This acid is more soluble in water than the *cis* isomeride (0·81 g. per 100 c.c. at 17°). It yields a *monoanilide*, m. p. 138—142°, and a *dianilide*, m. p. 215—216°.

W. A. S.

Dialkylaminoalkylcamphors. FARBWERKE VORM. MEISTER, LUCIUS, U. BRÜNING, and M. BOCKMÜHL (D.R.-P. 376348; from *Chem. Zentr.*, 1924, i, 1103).—*Diethylaminoethylcamphor*,



$$C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot CH_2NEt_2\\ | \\ CO\end{matrix},$$

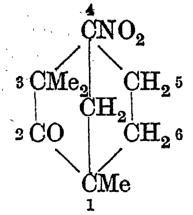
is an oil; the *hydrochloride* has m. p. 145°. *Dimethylaminoethylcamphor* is a yellow oil, b. p. 135—150°/10 mm.; *hydrochloride*, m. p. 231°.

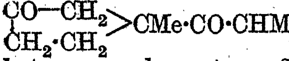
G. W. R.

Origin of Fenchol in Bouchardat and Lafont's Reaction. M. DÉLÉPINE (*Compt. rend.*, 1924, **178**, 2087—2089; cf. Bouchardat and Lafont, A., 1892, 199).—The action of benzoic and trichloroacetic acids on *d*-pinene and on *l*-pinene, respectively, results in formation of both fenchol and borneol derivatives in all four cases.

H. J. E.

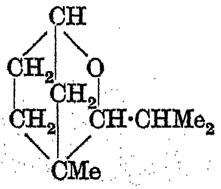
Nitrofenchones and some of their Reactions. S. NAMETKIN (*J. pr. Chem.*, 1924, [ii], **108**, 29—45).—By the action of nitric acid on fenchone, a *sec.*- and *tert.*-nitrofenchone were obtained by Konovalov (A., 1904, i, 257). These products have been further investigated.

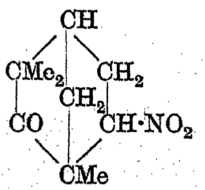


[With (Miss) W. CHOCHRJAKOV.]—The *tert.*-nitrofenchone has the annexed formula, instead of that given by Konovalov (*loc. cit.*). The reduction product with tin and hydrochloric acid is not a hydroxyfenchone, but a *diketone*, $C_{10}H_{16}O_2$, a colourless oil with a pleasant odour, b. p. 126·5—127°/11 mm., d_4^{20} 1·0028, n_D^{20} 1·4641 $[\alpha]_D$ —46·59° in alcohol. It forms a *disemicarbazone*, $C_{10}H_{16}(:N\cdot NH\cdot CO\cdot NH_2)_2$, decomp. 220°, and a *dioxime*, m. p. 123—124°. The diketone is reduced by sodium and alcohol to a *glycol*, $C_{10}H_{18}(OH)_2$, b. p. 151—152°/11 mm., $[\alpha]_D$ +44·54° in alcohol, giving a *diacetate*, b. p. 152—153°/12 mm., d_4^{20} 1·0189, n^{20} 1·4530. The dry glycol is converted by warm sulphuric acid into the *oxide*, $C_{10}H_{18}O$, b. p. 171—172°/749 mm., d_4^{20} 0·8985, n^{20} 1·4478; its formation is accompanied by that of other products. The formation of the diketone from the *tert.*-nitrofenchone involves the scission of one ring. The readiness with which the glycol forms an anhydride renders extremely probable the formula  $\begin{matrix}CO—CH_2\\ CH_2\cdot CH_2\end{matrix}\!\!>\!CMe\cdot CO\cdot CHMe_2$ for the diketone, scission having occurred between carbon atoms 3 and 4 of the fenchone ring. The oxide then has the formula I.

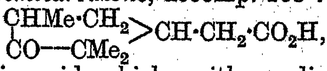
[With (Miss) K. LÜBOVZOV.]—The *sec.*-nitrofenchone, m. p. 88°, $[\alpha]_D$—42·88° in benzene, is a true nitro compound. With bromine in alkaline solution, it forms *bromonitrofenchone*, $C_{10}H_{14}O\cdot BrNO_2$, m. p. 53°. The only product of the acid reduction of *sec.*-nitrofenchone is a *ketonic acid*, $C_9H_{15}O\cdot CO_2H$, which begins to melt at 73°, forms a cloudy liquid at 76° and clears at 79—80°;

(I.)





(II.)

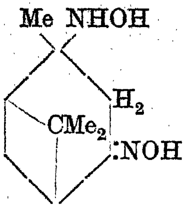
it forms a *semicarbazone*, decomp. 188°. This acid possibly has the structure  $\begin{matrix}CHMe\cdot CH_2\\ CO—CMe_2\end{matrix}\!\!>\!CH\cdot CH_2\cdot CO_2H$, and is related to *iso*camphoronic acid which, with αα-dimethyltricarballylic acid, is formed during the nitration of fenchone. *sec.*-Nitrofenchone probably has formula II.

By the action of nitric acid on camphenilone, two products are obtained, a liquid and crystals, m. p. 90—92°, apparently isomeric *nitro* derivatives. As a by-product, *iso*camphoronic acid was identified, and its formation supports the accepted formula for camphenilone.

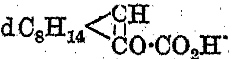
E. H. R.

Preparation of Monoalkylpulegones. A. HALLER and (MME.) P. RAMART (*Compt. rend.*, 1924, **179**, 120—122).—Pulegone in ethereal solution is treated first with an equimolecular quantity of powdered sodamide and then with the theoretical quantity of the requisite alkyl iodide, the alkylpulegone being finally isolated by distillation. The yields are low, owing chiefly to intermolecular condensation of the pulegone under the influence of the sodamide. The following compounds are described. *Methylpulegone*, b. p. 114°/19 mm., d_4^{23} 0·9256, $[\alpha]_D^{15}$ $-26{\cdot}24°$, *semicarbazone*, liquid; *ethylpulegone*, b. p. 117—121°/20 mm., d_4^{15} 0·9315, $[\alpha]_D^{15}$ $-25{\cdot}12°$, *semicarbazone*, m. p. 216°; n-*propylpulegone*, b. p. 127—131°/20 mm., d_4^{15} 0·9476, $[\alpha]_D^{15}$ $-22{\cdot}10°$, *semicarbazone*, m. p. 170°; iso*butylpulegone*, b. p. 128—132°/20 mm., d_4^{15} 0·9225, $[\alpha]_D^{15}$ $-18{\cdot}28°$, *semicarbazone*, liquid; *allylpulegone*, b. p. 129—133°/20 mm., d_4^{15} 0·9399, $[\alpha]_D^{15}$ $-27{\cdot}86°$, odour resembling that of vetiver and ionone, *semicarbazone*, m. p. 196°.
F. G. M.

Chemistry of the Terpene Group. I. Formation and Transformations of Verbenone and Verbenol from Turpentine. H. WIENHAUS and P. SCHUMM (*Annalen*, 1924, **439**, 20—48).—The auto-oxidation of Grecian turpentine in air, very slow under ordinary conditions, but much more rapid in sunlight and in the presence of an appropriate catalyst, yields verbenol and verbenone. A resin acid, $C_{20}H_{30}O_2$, known to be formed by the oxidation of turpentine, was isolated. In the oxidation of pinene by means of colloidal osmium and oxygen (cf. Willstätter and Sonnenfeld, A., 1913, i, 1200) α-pinene takes up 1 mol. of oxygen and, from the acid, viscous liquid produced, *d*-verbenone is isolated; oxime, m. p. 119—120° (cf. Blumann and Zeitschel, A., 1913, i, 495, give m. p. 115°), semicarbazone, m. p. 208° (decomp.). Excess of hydroxylamine yields the *hydroxylamino-oxime* (annexed formula), decomp. 165° (170° with rapid heating). Catalytic reduction of verbenoneoxime using palladium and hydrogen gives only a resinous product when 1 mol. of hydrogen is used, but with 3 mols. the product is verbanylamine, which is obtained by similar reduction of verbanoneoxime. By the action of 15% hydrogen peroxide in methyl-alcoholic sodium hydroxide solution, *d*-verbenone yields an *oxide*, b. p. 115°/16 mm., m. p. 6·5°, d_4^{20} 1·0561, n_D^{20} 1·48312, *semicarbazone*, m. p. 220° (decomp.). The formation of this oxide is a typical reaction for αβ-unsaturated ketones and together with the formation of the hydroxylamine-oxime proves that the double bond in the ring is conjugated with the keto group. The presence of a CH_2 group adjacent to the carbonyl group follows from the easy formation of an oximino derivative. Oxidation of verbenone and its oxime with ozone yields pinonic acid. Catalytic reduction (with palladium and hydrogen) of verbenone yields *d*-verbanone, which on reduction with sodium yields verbanol, b. p. 100°/13 mm., m. p. 58°, and a *pinacone*, m. p. 211—212°, b. p. 250—254°/22 mm. Verbanone yields a *hydrazone*, m. p. 27°, b. p. 146°/22 mm., d_4^{27} 0·986, n_D^{27} 1·51743,



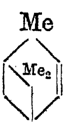
which at 140—160° yields pinane; *semicarbazone*, decomp. 230°; oxime, m. p. 88° (Blumann and Zeitschel, *loc. cit.*, give 77—78°), *hydrochloride*, m. p. 131°. Dilute sulphuric acid, (1 : 5, 1 : 2) regenerates the ketone from its oxime, but concentrated acid (1 : 1) yields a little *nitrile*, b. p. 230—236°, which is also obtained from the oxime by treatment with phosphorus pentoxide. Reduction of the nitrile with either sodium and alcohol, aluminium amalgam and moist ether, or platinum black and hydrogen, yields *verbanylamine*, b. p. 113—114°/20 mm., 211°/750 mm., d_4^{20} 0·9184, n_D^{20} 1·48125; *hydrochloride*, decomp. 245—250°; *nitrate*, decomp. 200°; *oxalate*, m. p. 131°. Concentrated mineral acids resinify verbanone, but by the action of 12% hydrochloric acid or 20% sulphuric acid it is converted into Δ^1-*o*-menthen-3-one, which on reduction by means of palladium black yields *o*-menthan-3-one. Reduction of verbanone by means of amalgamated zinc and 12% hydrochloric acid yields *o*-menthane, b. p. 169—170°/752 mm., d_4^{20} 0·8297, n_D^{20} 1·45649, $[\alpha]_D + 14·9°$, identical with that synthesised from *o*-tolyldimethylcarbinol (cf. Sabatier and Murat, A., 1913, i, 255). Fission of the six membered ring, leaving the four-membered ring intact, is accomplished by the action of sodamide and *iso*amyl nitrite on verbanone, which yields an *oximino* derivative, m. p. 140°. This on treatment with acetic anhydride yields the isomeric *imide* of the pinocamphoric acid obtained by Wallach and Engelbrecht (A., 1906, i, 684), m. p. 96°. Hydrolysis by means of dilute sodium hydroxide of either the oximino derivative or the imide yields the corresponding *amide*, m. p. 120°, which, unlike the amide of camphoric acid, is stable towards dilute alkalis. By means of the Grignard reaction verbanone yields the tertiary alcohol, *methylverbanol*, m. p. 187°, which yields a stable chromate sensitive to light. On distillation at ordinary pressure, or by heating with anhydrous oxalic acid the tertiary alcohol yields *homopinene*, b. p. 184—188°/748 mm., d_4^{20} 0·8538, n_D^{20} 1·47144, which shows considerable exaltation of molecular refraction. Like camphor, verbanone yields a white *additive* product on treatment with sodamide and carbon dioxide in anhydrous ether, which on acidification regenerates carbon dioxide and verbanone and is therefore an ester of the acid



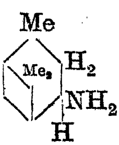
$C_8H_{14}<\begin{matrix}CH \\ \| \\ CO\cdot CO_2H\end{matrix}$.

The isolation of pure verbenol from the fraction, b. p. 130—150°/17 mm., of the product of auto-oxidation of Grecian turpentine is much more difficult. Catalytic reduction (palladium and hydrogen) of the crude verbenol yields crude verbanol, of which a fraction, b. p. 102°/20 mm., d_{20} 0·940, n_D^{20} 1·47618, forms a phthalate, m. p. 127°, and on oxidation by means of chromic acid and acetic acid yields pure verbanone.

Methyl verbanylxanthate, b. p. 100—110°/23 mm., on distillation yields a *hydrocarbon*, b. p. 156—159°/748 mm., d_4^{20} 0·8604, n_D^{20} 1·46672, $[\alpha]_D - 6·22°$, which is not α-pinene, since it yields a viscous red oil and not pinene hydrochloride on treatment with hydrochloric acid, and is probably δ-pinene (I), the preparation of which by the exhaustive methylation of verbanylamine (II) is in pro-



(I.)



(II.)

gress. Crude verbanol is probably a mixture of stereoisomeric alcohols. J. W. B.

Turpentines. G. DUPONT (*Ann. Chim.*, 1924, [x], **1**, 184—274).—An amplification and extension of previous work (cf. Dupont, A., 1922, i, 357; Vèzes and Dupont, A., 1922, i, 1042; Dupont, A., 1922, i, 1043; Dupont and Desalbres, A., 1923, i, 812; Dupont and Brus, A., 1923, i, 934; Dupont and Desalbres, A., 1923, i, 1215). Indian turpentine is characterised by its large proportion of Δ^3-carene and of longifolene, a sesquiterpene, whilst the percentages of pinene (24·8) and nopinene (9·7) are relatively small. The purest specimens of pinene obtained by the author from Aleppo turpentine had d^{15} 0·8620, n_D^{12} 1·4650, and $[\alpha]_D$ +48·08°, the velocity of crystallisation at −75° being 34 mm./min.; whilst the corresponding figures for pinene from Bordeaux turpentine were 0·8620, 1·4649, −46·65°, and 16·3 mm./min. The values for nopinene are 0·8740, 1·4872, and 196·5 mm./min. A study of the chemical properties of pinene and nopinene leads to the generalisation that if these two substances, by fixation of two atoms or groups, yield the same derivative, one of the entering groups must be a hydrogen atom. The following constants are given for Δ^3-carene: b. p. 170°, 70°/10 mm., d^{15} 0·8668, n_D^{25} 1·4675 (cf. Simonsen, T., 1920, **117**, 570). Hydrochloric acid acts on this substance, yielding a mixture of sylvestrene and dipentene hydrochlorides; potassium permanganate oxidises it to carene glycol, thence to *trans*-caronic acid. H. J. E.

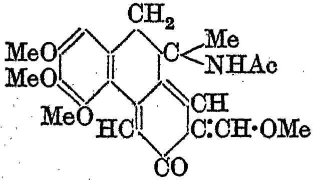
Transformations of Pinene by Acids. M. DELÉPINE (*Compt. rend.*, 1924, **179**, 175—178).—A discussion on the probable reactions occurring when pinene under the influence of acids—in particular of hydrochloric acid—is converted into esters of borneol, *iso*borneol, and fenchol, and also into camphene and limonene. F. G. M.

Essential Oils. SCHIMMEL U. CO. (*Report Schimmel u. Co.*, 1923, 1—240; from *Chem. Zentr.*, 1924, i, 2213—2215).—The following data are given for essential oils: essential oil from *Abies pindrow*, d^{15} 0·8655; α_D −10° 41′; n_D^{20} 1·47220; saponification number, *S.N.*, 0; esterification number, *E.N.*, 8·4; Brazilian rosewood oil, d^{15} 0·9120; α_D +6° 20′; n_D^{20} 1·47975; *S.N.*, 0; *E.N.*, 0; acetyl number, 131·6; American *Artemisia* oil, d^{15} 0·9575; α_D −0° 26′; n_D^{20} 1·47750; *S.N.*, 0·6; *E.N.*, 11·2; essential oil from *Nepeta cataria*, var. *citriodora*, Beck, d^{15} 0·8915; α_D −1° 34′; n_D^{20} 1·47485; *S.N.*, 5·6; *E.N.*, 8·4. G. W. R.

Constituents of Resins. X. Pinoresinol and the Natural Resin of Pine. A. ZINKE, A. ERBEN, and F. JELE (*Monatsh.*, 1924, **44**, 371—377).—The crystalline dibenzoate of pinoresinol, $C_{33}H_{28}O_8$, m. p. 159°, is more serviceable for the purification of the α-resin than Bamberger's process of crystallising the potassium salt. On hydrolysis with 10% alcoholic potassium hydroxide the pinoresinol is obtained, m. p. 120—121°. Oxidation of dibenzoylpinoresinol with chromic acid in acetic acid gives two new products, *A* and *B*, benzoic acid also being isolated. The yellow *substance* (*A*),

$C_{32}H_{24}O_{10}$, m. p. 219°, is evidently formed from the original resin by simultaneous loss of a methyl and formation of a carboxyl group. It gives an intense red solution in sodium hydroxide, and when it is heated benzoic acid is formed and a small quantity of oil distils, possessing a eugenol-like odour. The *substance B*, m. p. 148°, has the composition, $C_{20}H_{18}O_5$, and is also soluble in sodium hydroxide. It yields a *bromo* derivative, $C_{20}H_{17}O_5Br$, m. p. 155°. Pinoresinol gives a *di*-p-*bromobenzoate*, m. p. 231—232°, which on oxidation similarly yields two *products*, yellow plates, m. p. 245°, of the composition $C_{32}H_{22}O_{10}Br_2$, corresponding with product *A*, and reddish crystals, m. p. 169—171°, which contain halogen and are insoluble in sodium hydroxide. The structure of pinoresinol is discussed and a partial solution of the problem suggested. R. B.

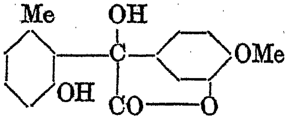
Constitution of Colchicine. A. WINDAUS (*Annalen*, 1924, **439**, 59—75).—The constitution of colchicine is deduced from its various decomposition products to be best represented by the annexed formula. Treated with concentrated hydrochloric acid, 1 mol. of acetic acid is split off yielding trimethylcolchicinic acid, which on heating with hydrogen iodide loses 3 mols. of methyl iodide and hence contains three methoxyl groups. With benzenesulphonyl chloride this acid yields a dibenzenesulphonyl derivative, existing in two isomeric forms, which on careful hydrolysis give the same *N*-benzenesulphonyltrimethylcolchicinic acid. This behaviour is explained by the presence of a hydroxymethylene group. When warmed for a short time with dilute hydrochloric acid, colchicine loses 1 mol. of methyl alcohol, yielding colchiceine, which, treated with a strongly alkaline solution of potassium iodide, yields a phenol, iodo-*N*-acetylcolchinol, $C_2H_{22}O_5NI$, by the replacement of a –CHO group by iodine, a reaction typical of aromatic hydroxymethylene or hydroxyaldehyde compounds. The presence of a methylene group is shown by the oxidation of colchicine with chromic anhydride to the ketone oxycolchicine; *semicarbazide*, m. p. 220—223°. Oxidation of colchicine, colchiceine, trimethylcolchicinic acid, or iodo-*N*-acetylcolchinol with potassium permanganate yields 3 : 4 : 5-trimethoxy-*o*-phthalic acid, whilst complete oxidation yields oxalic and succinic acids. Oxidation with hot potassium permanganate of the methyl ether of iodo-*N*-acetylcolchinol splits two of the six-membered rings, giving 5(?)-iodo-4-methoxy-*o*-phthalic acid. Reduction of the methyl ether with zinc dust gives *N*-acetylcolchinol methyl ether, which on energetic oxidation with chromic anhydride yields 4-methoxy-*o*-phthalimide, and hence the nitrogen atom is attached to the carbon atom next to the junction with the third ring. The methyl ether therefore contains three different six-membered rings, and since there are fifteen carbon atoms directly combined, it must be a derivative of methylanthracene or methylphenanthrene. *N*-Acetylcolchinol methyl ether, on treatment with methyl-alcoholic

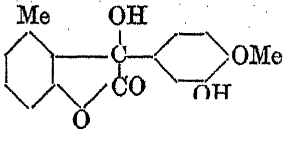


hydrochloric acid, yields colchinol methyl ether, which with 1 mol. of methyl iodide yields the *hydriodide* of N-*methylcolchinol methyl ether*, m. p. 244—245° (decomp.) (*picrate*, m. p. 200°), which with more methyl iodide yields the *hydriodide* of the *tertiary base*, m. p. 236° (decomp.) (*picrate*, m.p. 195—196°), and a *quaternary ammonium salt*, m. p. 231—232° (*picrate*, m. p. 193°), from which by means of silver oxide the *quaternary ammonium hydroxide* is obtained. This on heating in high vacuum yields trimethylamine, water, and 2:3:4:7-*tetramethoxy*-9-*methylphenanthrene*, m. p. 111°, which with hydrogen iodide yields the corresponding tetrahydric phenol, converted on distillation with zinc dust into 9-*methylphenanthrene*, m. p. 88—89°, identified by comparison with a specimen obtained by a rational synthesis. Colchicine is the methyl ether of colchiceine, which is the *N*-acetyl derivative of trimethylcolchicinic acid. Confirmation of these formulæ is obtained by catalytic reduction of colchicine and colchiceine. Each takes up 8 atoms of hydrogen, yielding *octahydrocolchicine*, m. p. 125—126°, and *octahydrocolchiceine*, m. p. 198—200°; *acetyl* derivative, m. p. 160—161°. Oxycolchicine similarly yields *octahydro-oxycolchicine*, m. p. 267—268°. J. W. B.

Phyllodulcin, a Sweet Principle of the Leaves of *Hydrangea Thunbergii*. S. H. MANIWA (*J. Pharm. Soc. Japan*, 1924, No. 507, 348—398; cf. *ibid.*, 1915, No. 406, 1399).—By extracting the leaves of the plant with alcohol three isomerides are obtained: *d*-phyllodulcin, m. p. 120°, $[\alpha]_D+67°$ to 69°; *d-iso*phyllodulcin, m. p. 131°, $[\alpha]_D+20°$; and *dl-iso*phyllodulcin, m. p. 131—132°. They contain one methoxy group, two hydroxy groups, and a lactone ring. By fusion with potassium hydroxide, phyllodulcin gives 3:4-dihydroxybenzoic acid and 3-hydroxy-*o*-toluic acid, $OH\cdot C_6H_3Me\cdot CO_2H$. The constitutions of phyllodulcin and *iso*phyllodulcin have been suggested by Asahina and Ueno (*ibid.*, 1916, No. 408, 146) to be (I) or (II):

(I.)





(II.)

The author has synthesised 3-hydroxy-*o*-toluic acid from aceto-*o*-toluidide and identified it with one of the decomposition products of phyllodulcin. Aceto-*o*-toluidide is nitrated to 3-nitro-*o*-toluidine, which is converted successively into a nitrile and an acid amide. By nitrous acid the amide is changed into 3-nitro-*o*-toluic acid, which is reduced, diazotised, and converted into 3-hydroxy-*o*-toluic acid, m. p. 168°. 3-*Methoxy*-o-*toluic acid* has m. p. 137—138° and the *ethoxy* compound, m. p. 126—127° (cf. Asahina and Kondo, *ibid.*, 1922, No. 482, 264). By heating *d*-phyllodulcin with potassium hydroxide, methyl iodide, and methyl alcohol in a sealed tube, d-*phyllodulcin dimethyl ether*, m. p. 87°, is produced. Its lactone ring is opened by heating with alcoholic potassium hydroxide, but is closed again by making the solution acidic. After opening the lactone ring of the dimethyl ether, it is oxidised with potassium permanganate in the presence of magnesium sulphate, 3-methoxy-*o*-toluic acid being produced. d-*Phyllodulcin diethyl ether* has m. p. 96—97°. By the same method, dl-*isophyllodulcin dimethyl ether*, m. p. 117°, and *diethyl ether*, m. p. 119—120°, give 3 : 4-dimethoxybenzoic acid and 3-ethoxy-4-methoxybenzoic acid, m. p. 166—167°, respectively. The last is prepared from 5-nitroguaiacol ethyl ether through the amino and cyano compounds. From these results, the constitutions of phyllodulcin and its isomeride are determined to be (I) and (II) respectively. The preparation of *iso*vanillic acid from anethole was attempted. 3-Nitroanisic acid, obtained from anethole by oxidising with nitric acid, is reduced to the amino compound with tin and hydrochloric acid. The hydrolysis of the diazo compound is accomplished with a concentrated sulphuric acid solution of cupric sulphate (D.R.-P. 167211), crystals, m. p. 213—214°, being produced, identical with 3 : 5-dihydroxy-4-methoxybenzoic acid (methyl ester, m. p. 95°) prepared from anisaldehyde. K. K.

Saponins. I. The Sapogenin of the White Soapwort (*Gypsophila sapogenin*). P. KARRER, W. FIORONI, R. WIDMER, and H. LIER (*Helv. Chim. Acta*, 1924, 7, 781—789; cf. Rosenthaler and Ström, A., 1912, i, 640).—The aqueous extract from *Radix saponaria levantica* was concentrated, heated with alcohol and sulphuric acid at 150°, and the sapogenin, termed by the authors *albsapogenin*, extracted with ether. Rosenthaler's formula, $C_{24}H_{34}O_5$ (*loc. cit.*), is rejected in favour of $C_{28}H_{44}O_4$. It yields a *methyl* ester, m. p. 192°, having begun to decompose at about 140°; an *oxime*, m. p. 264—265° (decomp.); a *semicarbazone*, m. p. 272° (cf. Rosenthaler, *loc. cit.*); and an *acetyl* derivative, sintering at 178° and melting at 192—194°. Albsapogenin may thus be formulated $C_{27}H_{42}O(OH)\cdot CO_2H$. When it is reduced by hydrogen and platinum black it yields (the ketonic group having been reduced) the dihydroxycarboxylic acid, albsapogenol, m. p. 321—322°; the *diacetyl* derivative sinters at 150°, m. p. 169°. Albsapogenin is oxidised by a cold mixture of chromic and acetic acids to *albsapogenic acid*, $C_{26}H_{41}O\cdot CO_2H$, m. p. 256°. When albsapogenin is heated with 80% sulphuric acid at 100—120° only 1 mol. of carbon monoxide is evolved, proving that it is an α-ketocarboxylic acid. When it is boiled with hydrochloric and acetic acids, or with sulphuric and acetic acids (although here another action takes place), but not with acetic acid alone, it is converted into *albsapin*, which is not an acid, but possibly a lactone. W. A. S.

Decomposition of Chlorophyllic Extracts. A. MAILHE (*Compt. rend.*, 1924, **178**, 1988—1990).—The alcoholic extract of plants after evaporation of the solvent ("chlorophyllic extract") was submitted to the action of anhydrous zinc chloride and magnesium chloride at various temperatures. Distillation with the latter substance at 300° yields a gas of the composition: carbon dioxide 57%, carbon monoxide 14%, hydrogen 20·5%, ethylenic hydrocarbons 9%. Simultaneously, a slightly acid liquid is obtained consisting of paraffins and ethylenic hydrocarbons. This was fractionated and from the fractions of higher boiling point, crystals of dinonyl ketone were deposited. The acidity of the distillate is due to partial hydrolysis of the catalyst. H. J. E.

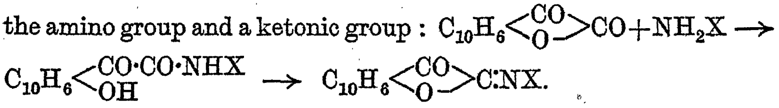
Hydrolytic Product of Chlorophyll containing Iron. S. Matysiak (D.R.-P. 376287; from *Chem. Zentr.*, 1924, i, 968).—Phæophytin free from magnesium, obtained by the hydrolysis of chlorophyll, is treated with ferric acetate. An amorphous, dark red *substance* is obtained which shows a biological similarity to hæmoglobin. It contains 2·53% of iron, and chars at 263° after sintering at 250°. G. W. R.

Bile Pigments. VIII. Mesobiliviolin, Mesobiliviolinogen, and the Condensation of Mesobilirubinogen with Aldehydes. Bisazo Pigment from Mesobilirubin. H. Fischer and G. Niemann (*Z. physiol. Chem.*, 1924, **137**, 293—316).—Mesobilirubin, m. p. 295—315°, is prepared by heating bilirubin with potassium methoxide and hydrazine in a closed tube at 180°. In alkaline solution, it is converted by atmospheric oxidation into mesobiliverdin and with ammoniacal copper solution it gives a crystalline *copper* salt. Mesobilirubin reacts with diazobenzenesulphonic acid, giving a violet pigment. On coupling it with diazobenzene chloride, a violet *pigment*, $C_{45}H_{48}O_6N_8,2HCl$, m. p. 192° (decomp.), is obtained. The methyl ester yields a similar bluish-grey *pigment*,

$$C_{47}H_{52}O_6N_8,2HCl,$$

m. p. 178° (decomp.). Mesobilirubinogen (A., 1911, i, 1005) gives a double *salt*, $C_{33}H_{44}O_6N_4,2FeCl_3$, when treated with ferric chloride and hydrochloric acid. *Mesobiliviolin*, $C_{33}H_{40}O_8N_4$, m. p. 215° (decomp.), is obtained by heating a suspension of this double salt in 4% hydrochloric acid on a water-bath; it separates in violet globules. With alcoholic zinc acetate, it shows a fluorescence characteristic of urobilin. On hydrogenation in alcoholic solution in presence of platinum, it yields *mesobiliviolinogen*, $C_{33}H_{48}O_5N_4$, fine prisms, m. p. 228—230°. In its properties it resembles mesobilirubinogen, giving an intense aldehyde reaction, but with zinc acetate it shows urobilin fluorescence only after some time. Mesobilirubinogen condenses with benzaldehyde in presence of hydrochloric acid giving a yellow monobasic *acid* (benzylidenebilirubic acid), $C_{24}H_{28}O_3N_2$, m. p. 240°. Its methyl ester, $C_{25}H_{30}O_3N_2$, m. p. 212—213°, is similar to, although not identical with, xanthobilirubin ester. On oxidation with concentrated nitric or chromic acid, the monobasic acid yields methylethylmaleinimide and benzoic acid, respectively. With *p*-nitrobenzaldehyde, mesobilirubinogen yields a similar condensation *product* (p-*nitrobenzylidenebilirubic* acid), $C_{24}H_{27}O_5N_3$, m. p. 253°. D. R. N.

Action of Oxalyl Chloride on Naphthols. M. Giua and V. De Franciscis (*Gazzetta*, 1924, **54**, 509—516).—4 : 5-Benzocoumaran-2 : 3-dione (cf. A., 1917, i, 204) may be obtained in good yield by heating on the water-bath a carbon disulphide solution of β-naphthol (1 mol.) and oxalyl chloride (1 mol.), and, when the evolution of hydrogen chloride tends to moderate, adding a small quantity of aluminium chloride. When this compound, suspended in alcohol, is treated with an organic base (1 mol.), the reddish-yellow diketone passes slowly into solution, giving a colourless or pale yellow liquid and sometimes a white precipitate, which is probably the substituted amide of the naphtholglyoxylic acid, formed by opening of the lactonic ring. When the action of the base and of heat is continued, the ring becomes closed again, with elimination of a molecule of water or alcohol and condensation of the amino group and a ketonic group:

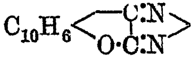


$$C_{10}H_6{<}\substack{CO\\O}{>}CO + NH_2X \rightarrow C_{10}H_6{<}\substack{CO{\cdot}CO{\cdot}NHX\\OH} \rightarrow C_{10}H_6{<}\substack{CO\\O}{>}C{:}NX.$$

4 : 5-*Benzocoumaran*-2 : 3-*dioneanil*,

$C_{10}H_6{<}\substack{CO\\O}{>}C{:}NPh$, obtained by the action of aniline on the diketone, forms yellow needles, m. p. 126—127° (slight decomp.), and gives an intense, deep red coloration with concentrated sulphuric acid. The o-*methylanil*, $C_{19}H_{13}O_2N$, prepared by means of *o*-toluidine, has m. p. 166—167°.

4 : 5-*Benzocoumarophenazine*,



$C_{10}H_6{<}\substack{C{:}N\\O{\cdot}C{:}N}{>}C_6H_4$, prepared by the action of *o*-phenylenediamine on 4 : 5-benzocoumaran-2 : 3-dione, forms orange-yellow needles, m. p. 286—287°.

4 : 5-Benzocoumaran-2 : 3-dione forms a *picrate*, $C_{18}H_9O_{10}N_3$, m. p. 109°; a *monosemicarbazone*, $C_{13}H_9O_3N_3$, m. p. 240—241°; and a *monophenylhydrazone*, $C_{18}H_{12}O_2N_2$, m. p. 226—227°.

Ethyl 2 : 1-*naphtholglyoxylate phenylosazone*,

$$OH{\cdot}C_{10}H_6{\cdot}C({:}N_2HPh){\cdot}C({:}N_2HPh){\cdot}OEt,$$

obtained by the action of phenylhydrazine (2 mols.) on 4 : 5-benzocoumaran-2 : 3-dione, forms white needles ($+C_6H_6$), m. p. (rapid heating) 165—166° (slight decomp.).

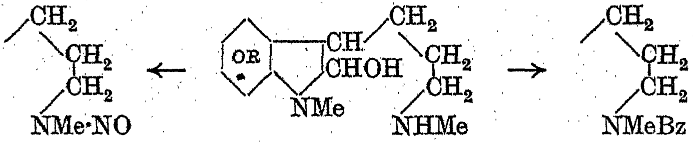
6 : 7-*Benzocoumaran*-2 : 3-*dione*, obtained in small yield from α-naphthyloxalyl chloride, has m. p. 146—147° (decomp.). When treated with *o*-phenylenediamine, it yields 6 : 7-*benzocoumarophenazine*, garnet-red needles, m. p. 232—233°. T. H. P.

Colouring Matter of the Blue Pansy ["Emperor William"]. G. S. CURREY (*Proc. Roy. Soc.*, 1924, **B**, **96**, 374—382).—The petals of the blue pansy, "Emperor William," are shown to contain violanin (6·3%, as potassium salt, of dried petals). The pigment (crystalline chloride) was deep ruby-red, as stated by Everest (A., 1918, i, 420). Rutin (9·68%) was also isolated, but as the presence of myricetin or cyanidin was not detected, no further evidence is obtained that an anthocyan pigment is formed within a flower by reduction of the corresponding flavonol pigment (cf. Everest and Hall, A., 1921, i, 485). A. J. H.

Degradation of Hydrogenated Derivatives of Eserine. M. and M. POLONOVSKI (*Compt. rend.*, 1924, **179**, 178—181; cf. A., 1923, i, 700, 831, 939, 940).—Hydroetheserolene, prepared by the reduction of etheserolene either with zinc and hydrochloric acid or with colloidal palladium or platinum in neutral or acid solution, has now been purified by conversion into the *hydrochloride*,

$C_{14}H_{19}ON,HCl$, m. p. 177°. The regenerated pure base has $[\alpha]_D$ $+3°$ in 95% alcohol, and $+35°$ in light petroleum, but undergoes inversion in acids, having $[\alpha]_D$ $-31°$ in dilute hydrochloric acid. *Hydroeseretholmethine methiodide*, m. p. 140° (zinc chloride *additive* compound, m. p. 263°), when warmed in concentrated solution with sodium hydroxide undergoes two simultaneous changes, losing methyl iodide to give hydroeseretholmethine, and losing trimethylamine hydriodide to give hydroetheserolene (*chlorozincate*, m. p. 248°). It is concluded that reduction of etheserolene to hydroetheserolene does not involve the saturation of an ethylenic linking present in the former, and two possible constitutional formulæ for each of the two bases are suggested. F. G. M.

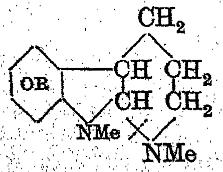
Nitroso and Benzoyl Derivatives of Eserine. M. and M. Polonovski (*Compt. rend.*, 1924, **179**, 334—336; cf. A., 1923, i, 831).—Eserine and eserethole can react as secondary bases in the formation of nitroso and benzoyl derivatives. By the addition of a concentrated solution of sodium nitrite to eserine dissolved in a slight excess of acetic acid, *nitrosoeserine* (II) is obtained as a yellow, neutral oil. Similarly, eserethole yields *nitrosoeserethole*, a viscous, neutral, optically inactive oil, soluble in dilute acids, but which forms no crystalline salts except the *picrate*, m. p. 133—134°. By the Schotten-Baumann reaction on eserethole suspended in dilute sodium hydroxide, *benzoyleserethole* is obtained as a viscous mass which is pulverisable in the presence of ether and petroleum, ($[\alpha]_D$ $-51°$). The formation of these derivatives can only be explained on the open-chain formula for eserine ("eserinol," I) (cf. this vol., i, 980) in accordance with the scheme:



(II.) (I.)

When an eserine salt is decomposed in aqueous solution by sodium hydrogen carbonate, an eserine *hydrate*, $C_{15}H_{21}O_2N_3,H_2O$, m. p. 82°, is obtained. This compound, however, is not regarded as having the eserinol structure. J. W. B.

Hydrogen Derivatives of Eserine. M. and M. Polonovski (*Compt. rend.*, 1924, **178**, 2078—2081).—A correction to previous work (A., 1923, i, 831). The formula previously suggested for eserine (quoted with an obvious misprint) with an ethylenic linking in the pyrrole nucleus is untenable, principally because the quaternary salts can combine with but 1 mol. of hydrogen, giving a completely saturated open-chain methine base, although other evidence also is adduced. The new formula suggested is appended. Reduction in acid solution is then explicable only on the assumption that the ring is opened, at the point indicated by the dotted line, as in the



case of the reduction of the quaternary salts. This view is supported by a reaction with methyl iodide towards which hydroeserethole behaves as a secondary open-chain base. L. J. H.

Quebrachamine. (MISS) E. FIELD (*J. Chem. Soc.*, 1924, **125**, 1444—1450).—This alkaloid, now being prepared commercially from quebracho bark (presumably as a by-product in the manufacture of aspidospermine), has been investigated in the hope of discovering some relationship between it and quebrachine and aspidospermine (from the same bark). Cow (*J. Pharm. Exp. Ther.*, 1913—1914, **5**, 341) has found their physiological actions to be similar and to differ only in intensity. Quebrachamine, $C_{19}H_{26}N_2$, has m. p. 147° (cf. Hesse, A., 1882, 742), $[\alpha]_D$ −109·5° in acetone, and distils without appreciable decomposition under high vacuum at 240—250°. It is feebly basic and forms a *sulphate*, $C_{19}H_{26}N_2,H_2SO_4,2H_2O$, sparingly soluble in cold water; the *oxalate* has m. p. 217°. The base appears to be fully saturated, and does not absorb hydrogen in the presence of colloidal platinum. It is apparently a monoacidic tertiary base; the *methiodide* has m. p. 234°, the *methosulphate* m. p. 235°. The nature of the second nitrogen atom has not been definitely ascertained; attempts to methylate it resulted in tarry products. Its behaviour towards nitrous acid suggests that it may be in the form of an imino group. On adding a solution of sodium nitrite to quebrachamine in acetic acid, a green oil is precipitated, changing to a yellow, amorphous solid. Attempts to form phenylcarbimido and acetyl derivatives were unsuccessful. The colour reactions of quebrachamine suggest that it contains an indole grouping. Quebrachamine *picrate*, m. p. 195—196°, exhibits chromoisomerism.

These properties are in harmony with the presence of a non-basic imino group and a benzene ring. The existence of the latter is indicated by the formation of picric acid when the alkaloid is heated with 30% nitric acid at 150°. Other oxidising agents react readily, but the products are amorphous mixtures. Bromine reacts with quebrachamine to form an unstable *perbromide*, $C_{19}H_{24}N_2Br_6$, m. p. 160° (decomp.), which, on prolonged boiling with water, loses bromine to give a *bromo* compound, $C_{19}H_{23}ON_2Br_3$, not melting at 290°. The compound is not changed by sodium hydroxide, and hence is not a hydrobromide. On boiling with sodium in alcoholic solution, quebrachamine is regenerated.

The high hydrogen content of the alkaloid precludes the presence of more than one benzene ring. A striking resemblance between the molecular formulæ of quebrachamine and aspidospermine ($C_{22}H_{30}O_2N_2$) is pointed out. Hydrolysis of the latter (cf. Ewins, T., 1914, **105**, 2738) causes the removal of a methoxyl and a *N*-acetyl group and leaves a base, aspidosine, $C_{19}H_{26}ON_2$, a phenolic substance, of which the parent substance, $C_{19}H_{26}N_2$, has the same empirical formula as quebrachamine. Aspidosine, like quebrachamine, is a monoacidic tertiary base and contains an imino group and a benzene ring. On the other hand, quebrachamine cannot be acetylated, and forms only a monomethiodide, whilst both nitrogen atoms in deacetylaspidospermine undergo methylation. Further, aspidospermine and its derivatives do not give the reactions of indoles. Attempts to remove the hydroxyl group from aspidosine were unsuccessful. No similar relationship between quebrachamine and quebrachine (yohimbine) is apparent, and reasons are given to show they can not have the same skeleton. A. C.

Spectrographic Study of Vegetable Alkaloids. Absorption of Ultra-violet Rays by Alkaloids of the *iso*Quinoline and Morphine Groups. P. Steiner (*Bull. Soc. Chim. biol.*, 1924, **6**, 231).—A detailed study of the ultra-violet absorption spectra of the principal *iso*quinoline and morphine alkaloids and of the compounds from which they are derived. The results of earlier work on the absorption spectra of some of these alkaloids is in general confirmed and a large amount of new quantitative data is presented.

Each alkaloid examined has a definitely characteristic ultra-violet absorption spectrum, which is closely related to that of the principal aromatic nucleus in the molecule when that nucleus is comparatively little modified (*e.g.*, the *iso*quinoline nucleus in papaverine). On the other hand, when the principal nucleus is much modified, the spectrum of the alkaloid is quite unlike that of the nucleus (*e.g.*, *iso*quinoline and berberine). When the molecule is made up of two large aromatic nuclei, its spectrum is determined almost entirely by one of them.

The author has specially investigated cotarnine and hydrastinine with a view to decide between the three structural formulæ which have been proposed for these substances. The absorption curves provide strong evidence that cotarnine has the ·CH(OH)·NMe· structure in hexane and ether solutions, thus confirming the conclusions of Dobbie, Lauder, and Tinkler (cf. T., 1903, **83**, 598), and that it has the ·CH:NMe(OH)· structure in aqueous and acid solutions; in alcoholic solution it is apparently a mixture of these two types. There is no evidence for the aldehydic formula.

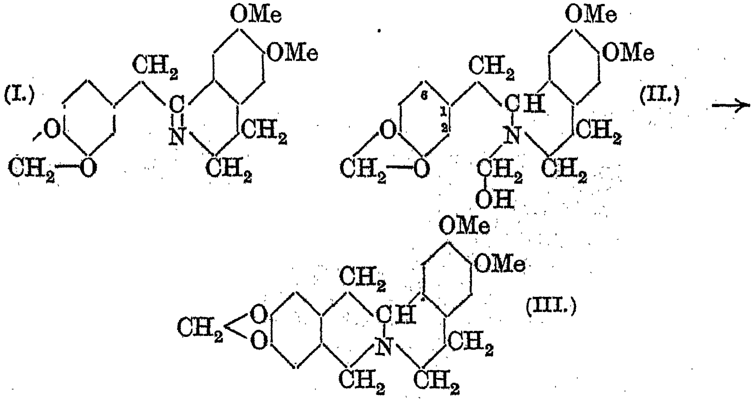
The alkaloids can be identified and determined by means of their absorption spectra, but the method has been worked out only for solutions of the pure substances. C. T. G.

Preparation of a Mercury Quinine Compound. Farbwerke vorm. Meister, Lucius, & Brüning (Swiss Pat. 100410; from *Chem. Zentr.*, 1924, i, 2206).—A solution obtained by shaking a suspension of mercuric oxide with quinine sulphate solution is added to ethyl alcohol, whereby a precipitate of *mercuriated quinine disulphate* is obtained. G. W. R.

ψ-*epi*Berberine. J. S. Buck and W. H. Perkin, jun. (*J. Chem. Soc.*, 1924, **125**, 1675—1686).—As *epi*berberine has hitherto been obtained only from cryptopine (T., 1918, **113**, 492), its synthesis was attempted by a method resembling that for berberine (cf. Pictet and Gams, A., 1911, i, 807), and 1-*homopiperonyl*-6 : 7-*dimethoxytetrahydro*iso*quinoline* was obtained, but the alkaloid produced from it by the action of formaldehyde and hydrochloric acid was shown to be *tetrahydro-ψ*-epi*berberine*, instead of tetrahydro*epi*berberine.

For preparation of the starting materials, veratraldehyde from vanillin was condensed with ethyl acetate in presence of sodium to 3 : 4-*dimethoxycinnamic* acid, which was reduced by sodium amalgam to 3 : 4-dimethoxyphenylpropionic acid (cf. Perkin and Robinson, T., 1907, **91**, 1079). The acid was converted by dry ammonia at 220—230° into its *amide*, m. p. 121°, which with sodium hypochlorite gave a 70% yield of homoveratrylamine (cf. Decker, A., 1913, i, 272). Condensation of piperonal with hippuric acid gave the azlactone, which was hydrolysed to benzoic acid and piperonylpyruvic acid (Kropp and Decker, A., 1909, i, 248), and oxidation of the latter with hydrogen peroxide (cf. Mauthner, A., 1910, i, 115) yielded homopiperonylic acid.

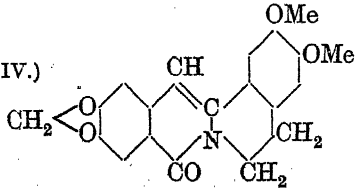
Homopiperonoylhomoveratrylamine, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_3(OMe)_2$, needles, m. p. 130—131°, was prepared (*a*) by heating homopiperonylic acid with homoveratrylamine at 180—200°, or (*b*) by addition of homopiperonyl chloride (prepared by use of thionyl chloride) to homoveratrylamine in presence of potassium hydroxide. Digestion with phosphorus oxychloride in boiling toluene gave a phosphate, from which alkali liberated 1-*homopiperonyl*-6 : 7-*dimethoxy*-3 : 4-*dihydro*iso*quinoline* (yield 80%) (I.) It is a strong base (colourless *hydrochloride*, m. p. 200°; *picrate*, m. p. 197°); except when pure and dry, it is oxidised by air to a *base*, $C_{19}H_{17}O_5N$, m. p. 152°. Reduction with sulphuric acid and zinc forms 1-*homopiperonyl*-6 : 7-*dimethoxytetrahydro*iso*quinoline*, irregular plates, m. p. 96° (a strong base, forming colourless *hydrochloride* and *sulphate*). Condensation of this substance with methylal was unsuccessful (cf. Pictet and Gams, *loc. cit.*), but its methyl-alcoholic solution was condensed with formaldehyde in presence of sodium hydrogen carbonate and the product (II) was treated with hot concentrated hydrochloric acid. The *hydrochloride* of *tetrahydro-ψ-*epi*berberine* was isolated and was decomposed with potassium carbonate, giving the *base*, jagged prismatic needles, m. p. 160—161° (III). It is distinguished from tetrahydro*epi*berberine by the m. p. and by the mixed m. p. The *picrate* melts at 149—150° (decomp.).

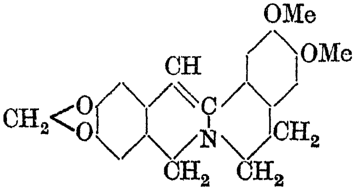

(I.) (II.) (III.)

No trace of tetrahydro*epi*berberine was formed, showing that ring formation (II ⟶ III) takes place solely with the hydrogen atom in position 6, and not with that in position 2.

Tetrahydro-ψ-*epi*berberine was oxidised by iodine in alcoholic solution, in presence of sodium acetate, and the resulting periodide was decomposed with sulphurous acid, yielding ψ-epi*berberinium iodide*, $C_{20}H_{18}O_4NI$, yellow, rhombic prisms, m. p. about 303°. Digestion of the iodide with silver chloride gave ψ-epi*berberinium chloride*, yellow, existing in 3 modifications: $C_{20}H_{18}O_2NCl,4\frac{1}{2}H_2O$, $C_{20}H_{18}O_4NCl,2\frac{1}{2}H_2O$, and the dimorphous anhydrous salt. The *chloroplatinate* and dimorphous *picrate*, m. p. 105°, were obtained. Decomposition of the chloride with potassium hydroxide is exactly analogous to the decomposition of *epi*berberinium chloride (T., 1918, **113**, 517). The products are (*a*) *oxy-ψ-*epi*berberine* (IV), almost colourless, m. p. 206°, differing from oxy*epi*berberine by its m. p., and (*b*) *dihydro-ψ-*epi*berberine* (V), yellow, rhombic prisms, m. p. 173°, distinguished from dihydro*epi*berberine by their mixed m. p. It forms pale yellow salts; *hydrochloride*, m. p. 266°; *hydriodide*, m. p. about 281°, with blackening. F. M. H.

(IV.)





(V.)

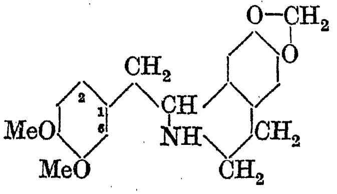
ψ-**Berberine.** R. D. Haworth, W. H. Perkin, jun., and J. Rankin (*J. Chem. Soc.*, 1924, **125**, 1686—1701).—Repetition of a synthesis by Pictet and Gams (A., 1911, i, 807) showed that the product of the action of methylal and hydrochloric acid on 1-veratryl-6 : 7-methylenedioxytetrahydro*iso*quinoline is not, as they concluded, tetrahydroberberine, but *tetrahydro-ψ-berberine.* Their synthesis of oxyberberine (A., 1911, i, 483) could not be repeated.

Starting materials were prepared as follows: 3 : 4-dimethoxyphenylpyruvic acid, yield 50%, obtained by a modification of Kropp and Decker's method (A., 1909, i, 248), gave 3 : 4-dimethoxyphenylacetic acid (Cain, Simonsen, and Smith, T., 1913, **103**, 1036). A pyridine solution of piperonal and malonic acid in presence of piperidine gave 3 : 4-methylenedioxycinnamic acid (quantitative yield), which furnished 3 : 4-methylenedioxyphenylpropionic acid (yield 85%) (Perkin and Robinson, T., 1907, **91**, 1079). The *amide* was prepared from the acid chloride and was converted into 3 : 4-methylenedioxyphenylethylamine (cf. Decker, A., 1913, i, 272).

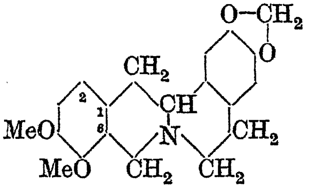
The yield of homoveratroylhomopiperonylamine was greatly improved; it was obtained (*a*) by condensation of 3 : 4-dimethoxyphenylacetyl chloride with 3 : 4-methylenedioxyphenylethylamine, or (*b*) by heating this amine with 3 : 4-dimethoxyphenylacetic acid at 180°. By boiling a toluene solution of homoveratroylhomopiperonylamine with phosphorus oxychloride, the yield (75%) of

1-*veratryl*-6 : 7-*methylenedioxydihydro*iso*quinoline* is much higher than when phosphoric oxide is used. Pictet and Gams (*loc. cit.*) describe the base as amorphous, m. p. 68—70°, salts indefinite. It is now found to be crystalline, m. p. 88° (*hydrochloride*, m. p. 62°, loses water of crystallisation and then melts at 125°; *hydriodide*, m. p. 239—240°; *picrate*, m. p. 206°). In air, it tends to oxidise to a *base*, $C_{19}H_{17}O_5N$, m. p. 151°. Reduction of the dihydro*iso*quinoline by means of tin and hydrochloric acid yielded 1-*veratryl*-6 : 7-*methylenedioxytetrahydro*iso*quinoline* (I), prisms, m. p. 84° (*hydrochloride*, prisms, m. p. 236°, *sulphate*, plates, m. p. 136—137°, *picrate*, yellow needles, m. p. 185—187°); this is analogous to similar tetrahydro*iso*quinolines, which all melt below 100°, but Pictet and Gams gave as m. p. of the base 208—210° and found the salts difficult to crystallise. When (I) is condensed with methylal and hydrochloric acid, it would be expected that III would be formed, but Pictet and Gams claim that they obtained *tetrahydroberberine* (II). This is especially anomalous, since condensation of 1-homopiperonyl-6 : 7-dimethoxytetrahydro*iso*quinoline has now been shown to occur normally (cf. Buck and Perkin, this vol., i, 1096). When 1-veratryl-6 : 7-methylenedioxytetrahydro*iso*quinoline was treated exactly as in the original synthesis, it gave a *base*, $C_{20}H_{21}O_4N$, small needles, m. p. 177°: but tetrahydroberberine melts at 169° and the mixture at 142—144°. Therefore this must be isomeric with tetrahydroberberine (II) and has been named *tetrahydro-ψ-berberine* (III) (*hydrochloride* darkens at 222°, m. p. 228—230°; *hydriodide* softens at 178°, m. p. 222°; *sulphate*, m. p. 168°; *picrate*, m. p. 176°; *methiodide*, prismatic needles, m. p. 256° [decomp. 260°]). The yield was small and an amorphous substance was produced containing no tetrahydroberberine. A much better yield (60%) of tetrahydro-ψ-berberine is obtained by condensing a methyl-alcoholic solution of the tetrahydro*iso*quinoline with formaldehyde and decomposing the formyl derivative with hydrochloric acid (cf. Decker, *loc. cit.*).

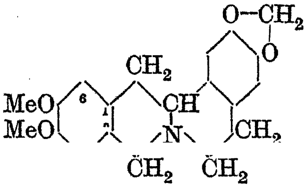
(I.)



(II.)



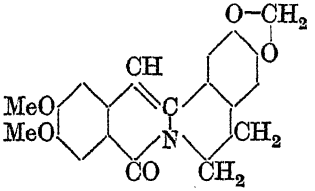
(III.)

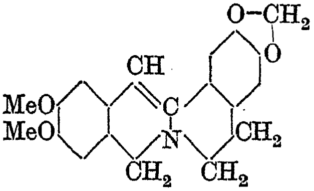


Tetrahydro-ψ-berberine is oxidised by iodine in alcoholic solution to *ψ-berberinium iodide*, canary-yellow needles, m. p. 274° (decomp.). Silver chloride converts this into *ψ-berberinium chloride*, obtained anhydrous from alcohol (darkens at 270°, decomp. 300°), from water as $C_{20}H_{18}O_4NCl,4\frac{1}{2}H_2O$ (*picrate*, decomp. 305°, whereas berberinium picrate melts at 239°).

When ψ-berberinium chloride is warmed with aqueous potassium hydroxide, there are obtained *oxy-ψ-berberine* (IV), almost colourless needles, m. p. 268°, mixed m. p. with oxyberberine, 184—186°, and *dihydro-ψ-berberine* (V), pale yellow needles, m. p. 165—167°, mixed m. p. with dihydroberberine, 141—143°, m. p. of *hydrochloride*, 253—255° (decomp.).

(IV.)

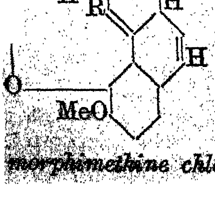




(V.)

The work by which Pictet and Gams claim to have synthesised oxyberberine was repeated. By condensing the hydrochloride of homopiperonylamine with methylal in presence of hydrochloric acid they obtained methylene-6 : 7-dioxytetrahydro*iso*quinoline (norhydrohydrastinine), as an oil, b. p. 197—199°/50 mm., m. p. of hydrochloride, 255—267°. Repetition now gave the *hydrochloride* (small yield, m. p. 275°), from which the crystalline *base*, m. p. 80—81°, was obtained. Decker and Becker showed that if methylal is replaced by formaldehyde, a good yield of methylenehomopiperonylamine is obtained and can be converted into norhydrohydrastinine (A., 1913, i, 291), so this method was adopted. Pictet and Gams converted crude norhydrohydrastinine into its *o*-nitrobenzoyl derivative, m. p. 104°, but the m. p. of this derivative, as prepared from the pure base, was now found to be 154°. Their next step was to condense it with methyl opianate and decompose with alcoholic potassium hydroxide, when it is stated that oxyberberine was formed. But on repeating the experiment, no trace of it could be isolated; it is moreover shown that when oxyberberine is treated with potassium hydroxide, under the conditions of the experiment of Pictet and Gams, it is completely decomposed to a phenolic substance. F. M. H.

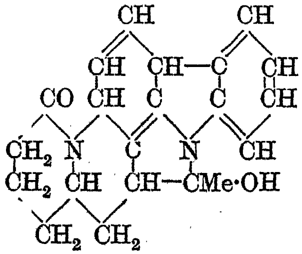
Constitution of Morphine. F. Faltis and A. Suppan (*Pharm. Monatsh.*, 1923, 4, 189—192; from *Chem. Zentr.*, 1924, i, 918—919).—Hydrogenation of either α- or β-dimethylmorphimethine yields the same product, four hydrogen atoms being absorbed. The two methine bases differ only in the position of the olefinic linkings. The annexed formula is suggested for β-dimethyldimorphimethine; it explains the relationship of the β- and ε-methines. *α-Tetrahydrodimethylmorphine*, $C_{20}H_{29}O_3N$, m. p. 43—46°, is obtained by the catalytic reduction of α-dimethylmorphimethine. *Tetrahydrodimethylmorphimethine chloroaurate* has m. p. 141—143° (decomp.). The



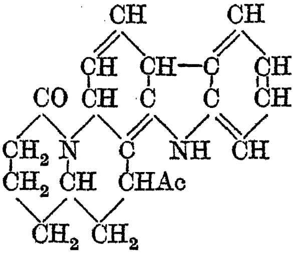
methiodide decomposes at 247°. β-*Dihydrodimethylmorphimethine*, obtained by partial reduction of the β-methine, has m. p. 115.° G. W. R.

Preparation of an Additive Product of Codeine. O. Hinsberg (D.R.-P. 377588; from *Chem. Zentr.*, 1924, i, 968).—Codeine and *p*-acetaminophenol yield an *additive* compound of composition $C_{18}H_{21}O_3N,OH\cdot C_6H_4\cdot NHAc$, m. p. 125°. G. W. R.

Constitutional Formula of Strychnine. III. E. Oliveri-Mandalà (*Gazzetta*, 1924, **54**, 516—528).—In the light of present knowledge concerning the reactions of strychnine and *iso*strychnine (cf. A., 1923, i, 702, 1223), the formulæ which best express the structures of these two bases are respectively,



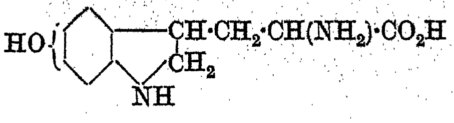
and

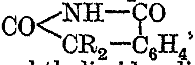


(cf. Perkin and Robinson, T., 1910, **97**, 305). T. H. P.

Preparation of Acyl*apo*cincholoiponitriles. A. Kaufmann (D.R.-P. 382911; from *Chem. Zentr.*, 1924, i, 1595—1596).—Acylcincholoiponamides are treated with alkali hypohalogenites. *Benzoylcincholoiponamide* (1-*benzoyl*-3-*ethylpiperidinoacetamide*), m. p. 88—89°, is converted by alkaline hypobromite into *benzoyl*-apo*cincholoiponitrile* (1-*benzoyl*-3-*ethylpiperidine*-4-*carboxylonitrile*). *Benzoyl*apo*cincholoiponamide* has m. p. 144°.

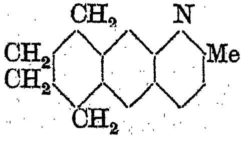
Isolation from Casein of an Amino-acid of the Indole Group with the Composition $C_{11}H_{14}O_3N_2$. E. Abderhalden and H. Sickel (*Z. physiol. Chem.*, 1924, **138**, 108—117).—The amino-acid previously isolated from casein and regarded as a hydroxytryptophan (Abderhalden and Kempe, A., 1907, i, 808) has been found to have the composition $C_{11}H_{14}O_3N_2,2\frac{1}{2}H_2O$. It has m. p. 146° (slow heating), $[\alpha]_D^{22}$ −28·68°, −28·10° (aqueous solution), and, from its colour reactions, is provisionally considered to be a hydroxydihydrotryptophan of the annexed structure. When dried at 105° in a vacuum over phosphorus pentoxide it loses its water of crystallisation and, at the same time, appears to lose further water with the formation of an anhydride. It forms a *dibenzoyl* derivative, decomposing at 136° after sintering at 72°. E. S.



Chemical Functions of Hypnotics, and of Hydantoin Derivatives in particular. A. Lumière and F. Perrin (*Bull. Soc. chim.*, 1924, [iv], **35**, 1022—1026).—The most active hypnotics known belong to the aliphatic series and contain a quaternary carbon atom linked to alkyl groups. The methyl derivatives are inactive, and the hypnotic effect appears to increase with replacement of methyl by homologous radicals, up to a solubility limit. Of the dialkylhomophthalimides,  $CO<\begin{matrix}NH-CO\\ CR_2-C_6H_4\end{matrix}$, obtained by the action of alkyl iodides on homophthalimide, diethylhomophthalimide, *ethylpropylhomophthalimide*, m. p. 117°, and *diallylhomophthalimide*, m. p. 140°, are hypnotic, whilst *dipropylhomophthalimide*, m. p. 128°, is inactive. Similarly, among the dialkylacetylacetamides, obtained by the action of alkyl halides on the amides in the presence of sodium ethoxide, the following order of hypnotic activity holds: acetyldiethylacetamide > *acetyldipropylacetamide*, m. p. 100° > *acetyldiallylacetamide*, m. p. 115° > *acetylethyl*iso*butylacetamide*, m. p. 108°. In view of the unpleasant effects sometimes produced by hypnotics such as "nirvanol" (phenylethylhydantoin) which contain an aromatic radical, a number of other derivatives of hydantoin have been prepared by warming dialkylcyanoacetamides with sodium hypochlorite. *Ethyl*iso*butylhydantoin*, m. p. 199°, *propyl*iso*butylhydantoin*, m. p. 173°, and especially dipropylhydantoin, m. p. 199°, are hypnotic, but not *di*-iso*butylhydantoin*, m. p. 220°.

R. B.

Course of the Quinaldine Synthesis with β-Aminotetrahydronaphthalene. J. LINDNER, M. DJULGEROWA, and A. MAYR (*Monatsh.*, 1924, **44**, 337—347).—Experiments on the course of the quinaldine synthesis with β-aminotetralin (*ar*-β-tetrahydronaphthylamine) show that both the linear and the angular compound are produced (cf. Braun and Gruber, A., 1922, i, 762), but the proportions could not be determined owing to the difficulty of separation. High concentrations of hydrochloric acid appeared to favour the synthesis, and from the reaction product after adding alkali, distilling in a vacuum, and removing unchanged β-tetrahydronaphthylamine as *benzoyl*-ar-β-*tetrahydronaphthylamine*, m. p. 167°, the two quinaldines are separated by fractional crystallisation of the picrates from water, or extraction of the hydrobromides with benzene or fractional precipitation of the hydrochlorides or hydrobromides in alcoholic solution with ether. 6 : 7-*Tetramethylenequinaldine* (annexed formula), m. p. 45°, obtained finally by decomposition of the picrate with ammonia and extraction with benzene, gives a hygroscopic *hydrochloride*, $C_{14}H_{15}N,HCl$, m. p. 209—212°, a *hydrobromide*, m. p. 212°, and a *picrate*, m. p. 206°.

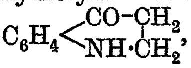


5 : 6-*Tetramethylenequinaldine*, m. p. 57°, was obtained similarly. The *hydrochloride*, $C_{14}H_{15}N,HCl$, m. p. about 240°, and *hydrobromide*, $C_{14}H_{15}N,HBr$, m. p. 220°, are non-hygroscopic and are less soluble than the isomeric compounds. The *chromate* is orange, but rapidly turns brown. The *picrate*, m. p. 190°, is less soluble in water than the picrate of the isomeric quinaldine, m. p. 170°. The constitution of the base is established by its dehydrogenation

at 700° to β-naphthoquinaldine, m. p. 81·5—82° (cf. Döbner and Miller, A., 1884, 1373).

In the preparation of β-aminotetrahydronaphthalene by Bamberger and Kitschelt's method (A., 1890, 631) a by-product, $C_{10}H_{12}N{\cdot}C_5H_{11}$, is produced, which is probably an amyl derivative of *ar*- or *ac*-tetrahydronaphthylamine. R. B.

Synthesis of 4-Tetrahydroquinolone and a new Synthesis of 4-Methoxyquinoline. G. R. Clemo and W. H. Perkin, jun. (*J. Chem. Soc.*, 1924, **125**, 1608—1622).—Condensation, in presence of alkali, of toluene-*p*-sulphonanilide and β-chloropropionic acid yielded *toluene*-p-*sulphonyl*-β-*anilinopropionic acid*, m. p. 144° (*methyl* ester, m. p. 61—62°). The yield of a *by-product*, $2C_{16}H_{17}O_4NS,H_2O$ (?), m. p. 213°, can be increased by varying the conditions. Toluene-*p*-sulphonyl-β-anilinopropionic acid was converted by phosphoric oxide in boiling xylene into *toluene*-p-*sulphonyl*-4-*tetrahydroquinolone*, m. p. 140—141°. Hydrolysis with hydrochloric acid liberated 4-*tetrahydroquinolone*,

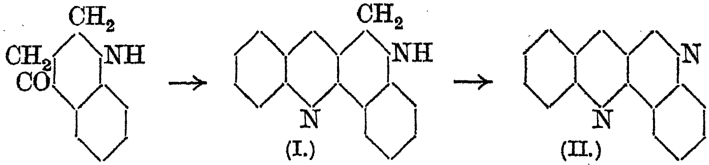


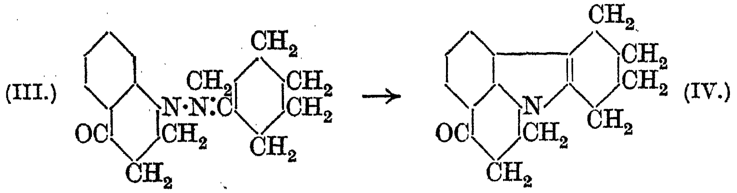
$C_6H_4{<}\begin{matrix}CO{-}CH_2\\ NH{\cdot}CH_2\end{matrix}$, b. p. 195°/20 mm., m. p. 144°.

The action of phosphoryl chloride on toluene-*p*-sulphonyl-β-anilinopropionic acid gave *toluene*-p-*sulphonyl*-3-*chloro*-4-*tetrahydroquinolone*, m. p. 124°. Since cold concentrated sulphuric acid eliminates hydrogen chloride, the chlorine atom cannot be situated in the benzene ring, whilst it cannot be attached to nitrogen because the substance does not react with diethylamine, diethylaniline, or potassium iodide. When boiled with concentrated hydrochloric acid, it is converted into 4-tetrahydroquinolone. Whilst toluene-*p*-sulphonyl-4-tetrahydroquinolone is converted by methyl-alcoholic potassium hydroxide into an *isomeric substance*, m. p. 135—150°, the corresponding derivative of 3-chloro-4-tetrahydroquinolone forms 4-*methoxyquinoline*, b. p. 167°/20 mm., m. p. 39—40°; *methiodide*, m. p. 145° (decomp.); *chloromercurate*, m. p. 201—202° (decomp.) (cf. Meyer, A., 1906, i, 604). Removal of the toluenesulphonyl group seems to be connected with the presence of the chlorine atom in the β-position adjacent to the carbonyl group; two suggestions as to the mechanism of the reaction are made.

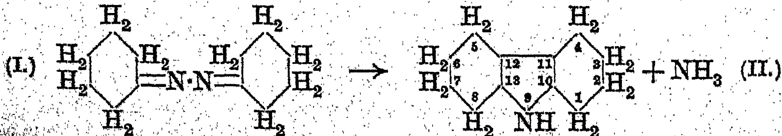
The NH: group of tetrahydroquinolone is in evidence since with nitrous acid it gives *nitroso*-4-*tetrahydroquinolone*, m. p. 98°; it gives a derivative with toluene-*p*-sulphonyl chloride, and with benzoyl chloride gives *benzoyl*-4-*tetrahydroquinolone*, m. p. 122°. The reactivity of the β-CH_2: group is shown by condensation with benzaldehyde in alcoholic solution, in presence of sodium hydroxide, to 3-*benzylidene*-4-*tetrahydroquinolone*, m. p. 214°. The CO: group is reactive and with phenylhydrazine there is formed 4-*tetrahydroquinolonephenylhydrazone*, m. p. 110°. On heating with dilute sulphuric acid, this undergoes the Fischer indole transformation with simultaneous oxidation, yielding 3 : 4-*quinindoline*, which melts and sublimes above 320° (*hydrochloride* and *chloroplatinate* described). When isatin and 4-tetrahydroquinolone are condensed and the product is heated under reduced pressure at

210°, carbon dioxide is eliminated, forming *dihydro*-2 : 3-*quinoquinoline* (I), m. p. 235—237° (softening at 230°), affording fluorescent solutions. Distillation over lead oxide affords 2 : 3-*quinoquinoline* (II), m. p. 186—187°. Reduction of nitroso-4-tetrahydroquinolone at 35—40° with zinc dust in presence of *cyclo*hexanone gave 1-cyclo*hexylideneamino*-4-*tetrahydroquinolone* (III), m. p. 112°. Dilute sulphuric acid converts this into *tetrahydrocarbazole*-9 : 8-*anhydropropionic acid* (IV), m. p. 135—136°; *phenylhydrazone*, m. p. 191°. 4-Tetrahydroquinolone is reduced by sodium amalgam to a mixture of 4-*hydroxytetrahydroquinoline*, colourless prisms, m. p. 83—84° (*diacetyl* derivative, m. p. 95—96°), and 4 : 4′-*dihydroxy*-1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-*octahydro*-4 : 4′-*diquinolyl*, decomp. 235°, clear melt at 260°. This pinacol is dehydrated by concentrated sulphuric acid to 1 : 2 : 1′ : 2′-*tetrahydro*-4 : 4′-*diquinolyl*, m. p. 165° (softening at 155°); *diacetyl* derivative, m. p. 230—231°. On boiling the methyl-alcoholic solution of the pinacol, oxidation occurs to 1 : 2-*dihydro*-4 : 4′-*diquinolyl*, m. p. 210° (softening at 200°); on keeping the solution in contact with air for some days, it yields 4 : 4′-*diquinolyl*, m. p. 166°. F. M. H.





1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-Octahydrocarbazole and its Derivatives. W. H. PERKIN, jun., and S. G. P. PLANT (*J. Chem. Soc.*, 1924, **125**, 1503—1512).—A detailed study of some of the more highly reduced derivatives of carbazole is described (see also T., 1921, **119**, 1825; 1923, **123**, 676). Catalytic reduction of carbazole by hydrogen in the presence of nickel does not appear to give the desired derivatives (cf. Padoa and Chiaves, A., 1908, i, 104; Von Braun and Ritter, A., 1923, i, 141). *cyclo*Hexylideneazine (I) was prepared from *cyclo*hexanone and hydrazine hydrate, and this on heating with hydrogen chloride in tetrahydronaphthalene gave a dark red oil. The fraction of b. p. 165—170°/15 mm. solidified



and yielded (28% of the theoretical) 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrocarbazole* (II), m. p. 102°. The method of synthesis gives the constitution. The *picrate* had m. p. 140°; 9-*acetyloctahydrocarbazole*, m. p. 73°, was easily hydrolysed. Prolonged reduction of the octahydrocarbazole (II) with tin and hydrochloric acid gives 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 13-*decahydrocarbazole* (III), m. p. 75°, in good yield; *picrate*, m. p. 210° (decomp.). This decahydrocarbazole could not be reduced further in the electrolytic cell. Octahydrocarbazole is completely reduced electrolytically to *dodecahydrocarbazole* (IV), $C_{12}H_{20}NH$, m. p. 65°; *picrate*, m. p. 187°. It is noteworthy that decahydrocarbazole (III) is not reduced to dodecahydrocarbazole by electrolysis. Octahydrocarbazole (II) probably passes into 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 11-decahydrocarbazole and thence to (IV). Octahydrocarbazole is readily alkylated in alcoholic solution. When boiled under reflux with methyl iodide, it gave 9-*methyloctahydrocarbazole* (V), b. p. 139—140°/14 mm. (70% yield); *picrate*, m. p. 147°; *methiodide*, m. p. 194°. Reduction of (V), whether electrolytically or by tin and hydrochloric acid, produced only 9-*methyldecahydrocarbazole*, b. p. 128°/13 mm.; *picrate*, m. p. 162—163°; a definite methiodide was not obtained. 9-*Methyldodecahydrocarbazole*, b. p. 132°/18 mm., was prepared in good yield by the action of methyl iodide on (IV); *picrate*, m. p. 146°.

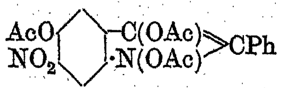
9-*Ethyloctahydrocarbazole*, prepared similarly, is a viscous, colourless oil, b. p. 166—170°/20 mm., which gradually turned yellow and then bright red on exposure to air; *picrate*, m. p. 152°; *methiodide*, m. p. 169°. 9-*Ethyldecahydrocarbazole* can be obtained by both of the methods given for the 9-methyl derivative as a colourless liquid, stable in air, b. p. 148—150°/21 mm.; *picrate*, m. p. 202°; *methiodide*, m. p. 205°. 9-*Ethyldodecahydrocarbazole*, by ethylation of dodecahydrocarbazole, has b. p. 143—145°/22 mm.; *picrate*, m. p. 132—133°; *methiodide*, m. p. 217°.

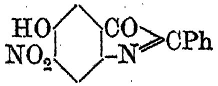
Several of these *N*-alkyl derivatives of the carbazoles were compared with corresponding compounds obtained by Von Braun and Ritter (*loc. cit.*) by catalytic reduction, and found to differ in important particulars: the 9-methyloctahydrocarbazole of Von Braun and Ritter has m. p. 94° and b. p. 176—178°/16 mm. and gives neither a crystalline picrate nor a methiodide (see above). The two compounds are isomerides, and it is suggested that the latter is 9-methyl-1 : 2 : 3 : 4 : 8 : 10 : 11 : 13-octahydro- or, more probably, 9-methyl-1 : 2 : 3 : 4 : 7 : 8 : 10 : 13-octahydrocarbazole, whilst that of the present authors has the true pyrrole structure and is 9-methyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrocarbazole. A similar structural difference is suggested for the corresponding isomeric decahydro compounds prepared by the two methods. The electrolytic reduction of tetrahydrocarbazole was found to stop at the hexahydro stage and to give the carbazole (m. p. 99°) in nearly quantitative yield. 9-*Methylhexahydrocarbazole* was obtained by reducing the tetra compound either electrolytically or by tin and hydrochloric acid. It is a colourless liquid, b. p. 144°/15 mm.; *picrate*, m. p. 143—144° (decomp.). A. C.

Sodamide as a Dehydrating Agent. Preparation of Indole, Methylindole, and Homologues. A. VERLEY (*Bull. Soc. chim.*, 1924, [iv], **35**, 1039—1040).—Sodamide readily converts aceto-*o*-toluidide into methylindole by heating at 270°, whereas the ordinary dehydrating agents, even thoria at 450°, fail; some *o*-toluidine is formed. The method is applicable to the preparation of homologues of methylindole. Indole can be obtained from formyl-*o*-toluidide, but the reaction must be moderated by dilution with sand or kieselguhr and the addition of a heavy solvent. R. B.

Hydroxyquinol Derivatives of the Isatogen Series. P. RUGGLI and W. LEONHARDT (*Helv. Chim. Acta*, 1924, **7**, 689—702; cf. A., 1923, i, 833).—6-*Nitro*-1 : 3 : 5-*triacetoxy*-2-*phenylindole*, m. p. 194—195° (I), is produced, together with another compound to be described later, when 6-nitro-2-phenylisatogen is treated with acetic anhydride and sulphuric acid, the action resembling that whereby *p*-benzoquinone is converted into 1 : 2 : 4-triacetoxybenzene. When the triacetoxy compound is heated with dilute alcoholic hydrochloric acid it affords 6-*nitro*-5-*hydroxy*-1 : 3-*diacetoxy*-2-*phenylindole*, m. p. 214—215°, which may be re-acetylated to regenerate its parent, or treated with chloroacetic anhydride to afford 6-*nitro*-1 : 3-*diacetoxy*-5-*chloroacetoxy*-2-*phenylindole*, m. p. 156—158° (decomp.). When the diacetoxy compound is treated with diazomethane, it gives 6-*nitro*-5-*methoxy*-1 : 3-*diacetoxy*-2-*phenylindole*, m. p. 221—222°. The triacetoxy compound dissolves in cold sulphuric acid to form a dark violet-coloured solution from which, on dilution, 6-*nitro*-5-*hydroxy*-3-*keto*-2-*phenylindolenine* (II), cherry-red needles, m. p. 188°, is precipitated. This substance yields an *oxime*, which decomposes at 280°, but when treated with methyl sulphate yields a *methyl* ether, m. p. 172°; this can be acetylated (on the phenolic hydroxyl) to an *acetyl* derivative, m. p. 152°. When 6-nitro-5-methoxy-1 : 3-diacetoxy-2-phenylindole is treated with concentrated sulphuric acid it yields 6-*nitro*-5-*methoxy*-3-*keto*-2-*phenylindolenine*, dark red needles, m. p. 157°; the *oxime*, m. p. 263—264°, can be methylated to a *methyl* derivative, m. p. 157°, which may also be obtained by treatment of the above hydroxy-oxime with an excess of diazomethane. The methoxyoxime is oxidised by chromic–acetic acid to 3 : 6-*dinitro*-5-*methoxy*-2-*phenylindole*, m. p. 303—306° (decomp.), whilst 6-nitro-5-methoxy-3-keto-2-phenylindolenine, the parent ketone, is converted by the same reagent into 4-*nitro*-2-*benzoylamido*-5-*methoxybenzoic acid*, m. p. 272°, which is hydrolysed by syrupy phosphoric acid at 130—170°, 4-*nitro*-2-*amino*-5-*methoxybenzoic acid*, violet needles, m. p. 217—218°, being thus obtained. 4-*Amino*-2-*benzoylamido*-5-*methoxybenzoic acid*, colourless scales, decomp. 200°, is obtained by catalytic reduction (nickel) of the nitro acid, and has an *acetyl* derivative, decomp. 275°; when it is diazotised and treated with cuprous oxide 2-*benzoylamido*-5-*methoxybenzoic acid*, m. p. 200°, is obtained. This

(I.)





(II.)

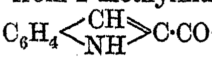
compound was identified by comparison with a sample prepared as follows. 2-*Nitro*-5-*methoxytoluene*, m. p. 50°, is obtained when 6-nitro-*m*-cresol is methylated; it is reduced and forthwith benzoylated yielding 2-*benzoylamido*-5-*methoxytoluene*, colourless needles, m. p. 200°, which, when oxidised with hot dilute potassium permanganate solution, yields 2-benzoylamido-5-methoxybenzoic acid. 2-*Benzoylamido*-3-*methoxybenzoic acid*, obtained *via* 2-nitro-3-methoxybenzoic acid, has m. p. 204·5°, and 2-*benzoylamido*-6-*methoxybenzoic acid* has m. p. 120°. The latter compound was prepared from 6-nitro-*o*-cresol; 2-*nitro*-6-*methoxytoluene* has m. p. 52° and when reduced and benzoylated yields 2-*benzoylamido*-6-*methoxytoluene*, m. p. 177°.

When 6-nitro-5-methoxy-1 : 3-diacetoxy-2-phenylindole is treated with stannous chloride in acetic acid solution 6-*amino*-5-*methoxy*-3-*acetoxy*-2-*phenylindole*, m. p. 212°, is obtained, and this is converted by acetic anhydride and sulphuric acid into a *diacetyl* derivative, m. p. 220°.

When methyl isatogenate (Pfeiffer, A., 1916, i, 327) is treated with acetic anhydride and a little sulphuric acid a *compound*, m. p. 193—195°, possibly analogous to the one described above, is obtained.

W. A. S.

Action of Oxalyl Chloride on certain Cyclic Organic Bases. M. Giua (*Gazzetta*, 1924, **54**, 593—597; cf. Oddo and Sanna, A., 1922, i, 371).—When oxalyl chloride and pyrrole interact below 0° and the mass is subsequently heated on a water-bath, black pigments are formed, together with 2-pyrrylglyoxyl chloride, which yields the acid (cf. Ciamician and Silber, A., 1884, 1044, 1193) in presence of water. From indole an almost theoretical yield of 2-indoleglyoxyl chloride is obtained in absolute ethereal solution, the corresponding acid being obtained by treatment with water; 2-methyl-3-indoleglyoxyl chloride and a magenta colouring matter are obtained similarly from 2-methylindole.



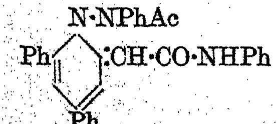
2-*Indoleglyoxyl chloride*, $C_6H_4{<}\substack{CH\\NH}{>}C{\cdot}CO{\cdot}COCl$, has m. p. 138—139°. 2-*Indoleglyoxylic acid*, $C_8H_6N{\cdot}CO{\cdot}CO_2H$, m. p. 224—225° (decomp.), when treated with fused potassium hydroxide at 200—205° yields indole-2-carboxylic acid. *Silver* 2-*indoleglyoxylate* forms white crystals.

2-*Methyl*-3-*indoleglyoxyl chloride* forms a brown, crystalline mass and, when heated with neutral solvents, resinifies and yields a magenta-red substance. 2-Methyl-3-indoleglyoxylic acid (cf. Angeli and Marchetti, A., 1908, i, 207) forms a *methyl* ester, m. p. 172—173°. The *colouring matter* formed together with the chloride separates as a dark red powder, m. p. about 120°, decomposes at a slightly higher temperature, dissolves readily in concentrated acids or in alkali solution, and contains 8·22% of nitrogen. T. H. P.

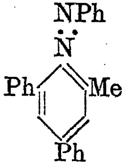
Pyridine-arylimines. I. W. Schneider [with W. Dornhardt, O. Süssenguth, H. Nitzsche, A. Ross, A. Sack, and E. Leutheusser] (*Annalen*, 1924, **438**, 115—146).—1 : 4 : 6-*Triphenyl*-2-*methylpyridinium iodide*, m. p. 243°, is obtained by treating

4 : 6-diphenyl-2-methylpyrylium iodide with aniline (cf. Schneider and Seebach, A., 1921, i, 877; Schneider and Ross, A., 1922, i, 1171); when treated with alkali, the corresponding anhydro base, 1 : 4 : 6-*triphenyl-2-methylenedihydropyridine*, is produced as an unstable, reddish-brown, amorphous substance; this combines instantly, when freshly isolated, with carbon disulphide to yield a dark red *substance*, $C_{50}H_{40}O_2N_2S_3$, m. p. 200° (cf. Schneider, Gaertner, and Jordan, this vol., i, 551), which gives a *perchlorate*, m. p. 170°. The anhydro base also combines with phenylthiocarbimide, affording a red *compound*, $C_{24}H_{19}N$,Ph·NCS, and with phenylcarbimide, an analogous *compound*, red prisms, m. p. 233°, being produced. 4 : 6-*Diphenyl*-1-*benzyl*-2-*methylpyridinium iodide*, similarly produced from benzylamine and the pyrylium iodide, has m. p. 212°. The corresponding base is again a brown, amorphous substance reacting with the above three reagents; with carbon disulphide a red *compound*, with phenylthiocarbimide a *compound*, red needles, m. p. 193°, and with phenylcarbimide a similar *product*, m. p. 195°, are obtained. 1-*Methylamino*-4 : 6-*diphenyl*-2-*methylpyridinium iodide*, obtained when methylhydrazine is used, forms yellow needles, m. p. 180°. Its anhydro *base* is very unstable; with carbon disulphide it affords a red substance and with phenyl-carbimide and -thiocarbimide greenish-yellow (m. p. 242°) and red (m. p. 164°) *compounds*, respectively. 1-*Phenylmethylamino*-4 : 6-*diphenyl*-2-*methylpyridinium iodide*, obtained by using *as.*-phenylmethylhydrazine, is an orange-yellow substance, m. p. 167°, and gives a yellow, amorphous *base* which, like its congeners, reacts with carbon disulphide and phenylcarbimide, but gives a definite *compound* (red needles, m. p. 171°) only with phenylthiocarbimide. Similarly, 1-*diphenylamino*-4 : 6-*diphenyl*-2-*methylpyridinium iodide* (yellow crystals, m. p. 137°) affords a yellow, amorphous *base*, very unstable, the phenylthiocarbimide *compound* of which forms dark red leaflets, m. p. 124°.

The characteristic properties of the methylenedihydropyridines are illustrated by the above examples. To the blue base obtained by Schneider and Seebach (*loc. cit.*) an analogous constitution was originally ascribed; certainly in some reactions it behaves as if it were 1-phenylamino-4 : 6-diphenyl-2-methylenedihydropyridine, but in other respects it is quite different from the above compounds of this class. Thus, it combines with phenylcarbimide, but with two molecular proportions, to form the *compound* $C_{38}H_{30}N_4O_2$, m. p. 128·4°; it also reacts with carbon disulphide, but slowly (cf. *loc. cit.*); it yields an *acetyl* derivative, an amorphous mass, resembling the above bases, which again combines with phenylcarbimide to a *compound*, m. p. 150° (annexed formula), and when treated with ammoniacal silver nitrate it forms a red complex *salt*, $(C_{24}H_{20}N_2)_2$,$AgNO_3$, m. p. 168°. On the other hand, the base is intensely blue and crystalline; when treated with methyl iodide it yields, as one product, the 1-phenylmethylamino-4 : 6-diphenyl-2-methylpyridinium iodide described above; its colour depends on



the solvent used to dissolve it, and its stability on the same factor; thus it is blue in benzene or chloroform and loses its colour in a few hours, but in alcohol it is violet and tolerably stable. Experiments are described in which the action of nitrous acid and nitric oxide on this base and on its congeners described below was investigated, but these gave no conclusive results. As the base obtained from 1-methylamino-4 : 6-diphenyl-2-methylpyridinium iodide, described above, resembles its congeners, in this blue base the presence of the phenyl group in place of the methyl is considered so to affect the valency distribution that the compound should be formulated as a pyridinephenylimine (annexed formula), being thus the first member of a new class of compounds. This explains satisfactorily the blue colour of the substance, and the properties wherein it resembles the methylene anhydro bases can be referred to tautomeric change.



Phenylhydrazine and 2 : 6-diphenyl-4-methylpyrylium iodide (Schneider and Ross, *loc. cit.*) yield, in cold alcohol solution with a little acetic acid, 1-*phenylamino*-2 : 6-*diphenyl*-4-*methylpyridinium iodide*, yellow needles, m. p. 200°. When this is treated with sodium hydroxide, 2 : 6-*diphenyl*-4-*methylpyridinephenylimine*, a deep blue substance, needles, m. p. 101°, closely resembling its isomeride, is obtained. This reacts with carbon disulphide and phenylthiocarbimide, and with phenylcarbimide forms an orange *compound* crystallising in leaflets, m. p. 152°. It also yields a complex *salt* with silver nitrate, m. p. 172°.

2 : 4 : 6-Triphenylpyrylium iodide (Schneider and Seebach, *loc. cit.*) and phenylhydrazine react in cold alcohol to give (α-) 2 : 4 : 6-*triphenylpyranol phenylhydrazide* (cf. following abstract), m. p. 162°, but in hot alcohol an isomeride, the (β-)*hydrazide*, m. p. 126°, is obtained. When the α-hydrazide is treated with hot acetic acid, and the solution basified, it is converted chiefly into 2 : 4 : 6-*triphenylpyridinephenylimine*, dark blue needles, m. p. 182°. This compound resembles its congeners, but is more stable, reacts more slowly, and gives less well-defined products with the customary reagents. When it is treated in dilute acetic acid solution with potassium iodide, 1-*phenylamino*-2 : 4 : 6-*triphenylpyridinium iodide*, yellow needles, m. p. 161°, is obtained, whilst with methyl iodide it yields 1-*phenylmethylamino*-2 : 4 : 6-*triphenylpyridinium iodide*, m. p. 136°, identical with the product of interaction of phenylmethylhydrazine and the pyrylium iodide. The corresponding amorphous anhydro *base* appears to suffer conversion into a *phenylhydrazide*, m. p. 160°, when recrystallised from alcohol (cf. following abstract). W. A. S.

Reaction of Pyrylium Compounds with Phenylhydrazine.

W. Schneider and W. Müller (*Annalen*, 1924, **438**, 147—154).—When 4 : 6-diphenyl-2-methylpyrylium iodide or sulphoacetate (cf. preceding abstract and earlier references quoted therein) is treated with phenylhydrazine in cold alcoholic solution, the α-phenylhydrazide, 4 : 6-*diphenyl*-2-*methylpyranolphenylhydrazide*, yellow needles, m. p. 119°, is obtained. In this compound, the pyranol ring is considered to remain intact. It is a comparatively unstable substance; even when dissolved in cold acetic acid it is partly decomposed to the parent pyrylium compound, and partly converted into a 1-phenylamino-4 : 6-diphenyl-2-methylpyridinium salt, whilst with alkali 4 : 6-diphenyl-2-methylpyridinephenylimine is obtained. With phenylhydrazine, or if the pyrylium salt be directly treated with an excess of phenylhydrazine, further interaction takes place, producing the *phenylhydrazone*,

$$NHPh\cdot N\colon CPh\cdot CH\colon CPh\cdot CH\colon CMe\cdot NH\cdot NHPh,$$

orange needles, m. p. 130°.

When the original alcoholic reaction mixture is heated, an isomeride, the β-*hydrazide*, is produced. This is also obtained when an alcoholic solution of the α-compound is heated for some time. It forms stable, brownish-yellow crystals, m. p. 115°. The pyranol ring is supposed here to have become opened up, but the authors have not yet decided which of the numerous possible formulæ should be attributed to the compound. It is only converted into the pyridinium salt by long treatment with acetic acid. When it is treated with phenylhydrazine, it yields a *phenylhydrazone* isomeric with that described above, yellow needles, m. p. 178°.

W. A. S.

4-Benzyl-2-methylquinoline. E. Rosenhauer (*J. pr. Chem.*, 1924, [ii], **108**, 91—98).—*4-Benzyl-2-methylquinoline*, obtained by heating *N*-benzylquinaldinium iodide at 230°, has m. p. 63°; *picrate*, decomp. 185°; *hydrochloride*, decomp. 216°; *hydriodide*, decomp. 234°; *methiodide*, decomp. 194°. The base reacts with benzaldehyde, forming *4-benzyl-2-styrylquinoline*, m. p. 99°; *picrate*, decomp. 237°; *hydrochloride*, decomp. 231°; *methiodide*, decomp. 224°. The methiodide when heated with alcoholic potassium hydroxide loses hydrogen iodide, forming 1-*methyl*-4-*benzylidene*-2-*styryl*-1 : 4-*dihydroquinoline*, brick-red needles, m. p. 140°.

4-*Benzyl*-2-p-*dimethylaminostyrylquinoline* forms yellow prisms, m. p. 158°; its halogen acid salts, which are dyestuffs, are of uncertain composition; the *picrate*, decomp. 239°, and *methiodide*, decomp. 261°, giving an intensely red alcoholic solution, were prepared. 4-*Benzyl*-2-m-*nitrostyrylquinoline*, crystals, m. p. 182°, forms a *picrate*, decomp. 217°. 4-*Benzylquinophthalone*, from 4-benzylquinaldine and phthalic anhydride, forms yellow needles, m. p. 236°.

E. H. R.

Aryl Substituted Aminoquinolines and their Derivatives. M. Dohrn, C. Zöllner, and Chemische Fabrik auf Aktien (vorm. E. Schering) (D.R.-P. 375715; from *Chem. Zentr.*, 1924, i, 967—968).—2-Arylquinoline-4-carboxylamides are treated with salts of hypohalogenous acids at low temperatures. The following compounds are mentioned: 4-*Amino*-2-*phenylquinoline*, m. p. 165°; 4-*amino*-2-*phenyl*-6-*methylquinoline*, m. p. 188—189°; 4-*amino*-2 : 2′-*chlorophenylquinoline*, m. p. 166°; 2 : 2′-*chlorophenylquinoline*-4-*carboxylamide*, m. p. 228—229°; 2 : 2′-*chlorophenylquinoline*-4-*carboxylic* acid, m. p. 256—257°; 2 : 4′-*chloro*-

phenylquinoline-4-carboxylic acid, m. p. 228—229°; 2 : 4′-*chlorophenylquinoline-4-carboxylamide,* m. p. 238°; and 4-*amino*-2 : 4′-*chlorophenylquinoline,* m. p. 150—151°. G. W. R.

Production of Acridinium Compounds. L. CASSELLA und Co. (Brit. Pat. 218542).—Hydroxy- and alkoxy-acridines are converted into acridinium compounds by the action of alkylating agents, such as methyl and ethyl *p*-toluenesulphonates, benzyl chloride, and ethylene chlorohydrin, in absence of bases, as, for example, in hot nitrobenzene solution. 3 : 6-*Dihydroxy*-10-*methylacridinium chloride,* yellow needles; 3 : 6-*dimethoxy*-10-*methylacridinium chloride,* light yellow scales; 3 : 6-*dimethoxy*-10-*ethylacridinium chloride,* orange-yellow scales, m. p. 198° (decomp.); 3 : 6-*dimethoxy*-10-*benzylacridinium chloride,* dark yellow needles, m. p. 236° (decomp.); and 3 : 6-*dimethoxy*-10-*hydroxyethylacridinium chloride,* pale yellow needles, m. p. 240—242°, are described, all of which are strong bactericides of low toxicity and slight tinctorial power. F. G. W.

Preparation of Colouring Matters. AKTIEN-GESELLSCHAFT FÜR ANILIN FABRIKATION (W. HERZBERG, and G. HOPPE) (D.R.-P. 384790; from *Chem. Zentr.*, 1924, i, 1110—1111).—The following compounds are mentioned: *hydroxynaphthacridine,* orange-yellow; its *hydrochloride,* yellow; and *dihydroxydinaphthacridine,* orange. G. W. R.

Unsymmetrical *CC*-Dialkylbarbituric Acids. E. LAYRAUD (Fr. Pat. 546997; from *Chem. Zentr.*, 1924, i, 2205; cf. this vol., i, 92—93).—The following compounds, obtained by alkylation of the silver compounds of monoalkylbarbituric acids, are described: *ethylbutylbarbituric acid,* m. p. 126—127°; *butylallylbarbituric acid,* m. p. 118°. G. W. R.

Unsymmetrical *CC*-Dialkylbarbituric Acids and their Salts. E. LAYRAUD (Fr. Pat. [Add.] 26209; from *Chem. Zentr.*, 1924, i, 2205—2206; cf. preceding abstract).—The following new compound is mentioned: *piperazine ethylbutylbarbiturate,* m. p. 150—155°. G. W. R.

Bromo Derivatives of 1-Methylglyoxaline and Constitution of "Chloroxalmethylin." I. E. BALABAN and F. L. PYMAN (*J. Chem. Soc.*, 1924, **125**, 1564—1572).—The bromination of 1-methylglyoxaline resembles that of glyoxaline (cf. T., 1922, **121**, 947). The main product is 2 : 4 : 5-tribromo-1-methylglyoxaline, m. p. 93—94·5° (*hydrochloride,* prisms, m. p. 190—200°). The second product was proved to be 4 : 5-*dibromo*-1-*methylglyoxaline,* m. p. 79—80°, by its preparation from 4 : 5-dibromoglyoxaline and methyl sulphate (*hydrochloride,* m. p. 179°, with previous softening [*dihydrate* also described], *nitrate,* m. p. 153°, *picrate,* m. p. 148—149°). Unlike the unmethylated base, 2 : 4 : 5-tribromo-1-methylglyoxaline is resistant to the action of sodium sulphite, so 4(or 5)-bromo-1-methylglyoxaline cannot be thus prepared. 5-*Bromo*-1-*methylglyoxaline,* b. p. 128°/*ca.* 15 mm.,

m. p. 45—46°, is obtained (yield 51%), together with 4-*bromo*-1-*methylglyoxaline* (yield 1·5%), by the action of methyl sulphate on 4(or 5)-bromoglyoxaline; the *hydrochloride* (losing $\frac{1}{2}H_2O$), m. p. 155°; *nitrate*, m. p. 155°; *hydrogen oxalate* (losing $\frac{1}{2}H_2O$), m. p. 147°; *picrate*, m. p. 190°, are described. Its nitration and sulphonation (as for 4-bromoglyoxaline, *loc. cit.*) gave 5-*bromo*-4-*nitro*-1-*methylglyoxaline* (yield 80%), m. p. 180° (*hydrochloride*, m. p. about 155°), and 5-*bromo*-1-*methylglyoxaline*-4(?)-*sulphonic acid* (yield 78%), m. p. 284°, hydrolysed to 5-*bromo*-1-*methylglyoxaline*. 5-Bromo-1-methylglyoxaline is converted by formaldehyde at 130° into 5-*bromo*-2-*hydroxymethyl*-1-*methylglyoxaline* (yield 42%), m. p. 143° (*picrate*, m. p. 165—166°). Reduction with hydriodic acid and phosphorus gave 1 : 2-dimethylglyoxaline (cf. Windaus, A., 1909, i, 258). Interaction of *sym*.-dimethyloxamide and phosphorus pentabromide gave 4 : 5-*dibromo*-1-*methylglyoxaline*. Contrary to the conclusion of Sarasin (A., 1923, i, 710), the product (chloroxalmethylin) of the interaction of *sym*.-dimethyloxamide and phosphorus pentachloride (Wallach, A., 1877, ii, 182) is found to be 5-*chloro*-1-*methylglyoxaline* and the isomeric base produced by distillation of its methiodide must therefore be 4-*chloro*-1-*methylglyoxaline*. The action of methyl iodide on 4(or 5)-bromo-1-methylglyoxaline gave 4(or 5)-*bromo*-1 : 3-*dimethylglyoxalinium iodide*, m. p. 202—204°, which by distillation in a vacuum yielded 4-*bromo*-1-*methylglyoxaline nitrate*, m. p. 155° (yield 43%); the *base* itself was an oil (*picrate*, m. p. 179°). Nitration and sulphonation of 4-bromo-1-methylglyoxaline gave 4-*bromo*-5-*nitro*-1-*methylglyoxaline* (yield 54%), m. p. 105°, this being the main product of the action of methyl sulphate on 4(or 5)-bromo-5(or 4)-nitroglyoxaline; 4-*bromo*-1-*methylglyoxaline*-5(?)-*sulphonic acid* (yield 77%), prisms ($+1H_2O$), m. p. 256° (decomp.), is hydrolysed to 4-*bromo*-1-*methylglyoxaline*.

4(or 5)-Bromoglyoxaline does not react with bromobenzene or sodium sulphite, but is reduced by hydriodic acid and phosphorus to glyoxaline. The reactivity of the halogen is increased by the presence of an *o*-nitro group. Thus 4(or 5)-bromo-5(or 4)-nitroglyoxaline on boiling with aqueous sodium sulphite gave 5(or 4)-*nitroglyoxaline*-4(or 5)-*sulphonic acid* (yield 88%), decomp. 300° (*sodium* salt described). The orientation of 5-chloro-(or bromo)-1-methylglyoxaline was established directly and that of 4-bromo-1-methylglyoxaline indirectly: "Chloroxalmethylin" *nitrate*, m. p. 145°, on heating with concentrated sulphuric acid, gave 5-*chloro*-4-*nitro*-1-*methylglyoxaline* (yield 71%), m. p. 147°. From 5-chloro-(or bromo)-4-nitro-1-methylglyoxaline was obtained 4-*nitro*-1-*methylglyoxaline*-5-*sulphonic acid*, m. p. 254° (*sodium* salt described). The latter was hydrolysed by 30% aqueous sulphuric acid at 170° to 4-*nitro*-1-*methylglyoxaline*. F. M. H.

Tautomerism of Amidines. IV. Methylation of 4(or 5)-Nitroglyoxaline and 4(or 5)-Phenylglyoxaline. C. E. Hazeldine, F. L. Pyman, and (the late) J. Winchester (*J. Chem. Soc.*, 1924, 125, 1431—1441).—The action of methyl sulphate on nitro-

and phenyl-substituted glyoxalines has been studied and the proportions of the two isomeric alkyl derivatives have been determined (cf. T., 1923, **123**, 3359). Glyoxalines having the nitro group in the 4(or 5)-position invariably yield the 5-nitro-1-methyl derivative as main product. The methylation of 4(or 5)-nitroglyoxaline leads to 5-nitro- and 4-nitro-1-methylglyoxalines in the proportions 350:1 (cf. also T., 1922, **121**, 2616; 1923, **123**, 494). The influence of the bromine atom is similar to, but not so powerful as that of the nitro group, the proportions for similar bromo-substituted compounds being 34 : 1. Substituents of negative polarity, methyl and cyanomethyl (cf. T., 1923, **123**, 367), act in the opposite way. The influence of phenyl as substituent is exceptional and 4(or 5)-phenylglyoxaline yields on methylation 4-phenyl- and 5-phenyl-1-methylglyoxaline in the proportions 4·8 : 1. On the other hand, the phenyl group affects the results of the distillation of the common methiodides in the same way as a nitro or bromo group. This abnormality may be ascribed more to the structure of the molecule than to its polarity. The orientation of the 4- and 5-nitro-1-methylglyoxalines was determined by the method used for the nitro-1 : 4- and -1 : 5-dimethylglyoxalines (cf. T., 1922, **121**, 2616). The differences in physical properties of the two monomethylnitroglyoxalines are paralleled by the above dimethyl derivatives. 4-*p*-Nitrophenyl- and 5-*p*-nitrophenyl-1-methylglyoxalines were obtained on nitrating the corresponding phenylmethylglyoxalines, the positions of the nitro groups being proved by the formation of a mixture of the two bases by the methylation of 4(or 5)-*p*-nitrophenylglyoxalines (T., 1921, **119**, 1893). Further nitration resulted in the formation of 5-nitro-4-*p*-nitrophenyl-1-methylglyoxaline, for which the position of the second nitro group was found by methylation of 4(or 5)-nitro-5(or 4)-*p*-nitrophenylglyoxaline. The dinitro base on reduction gave 5-amino-4-*p*-aminophenyl-1-methylglyoxaline, which on hydrolysis yielded *p*-aminophenylaminoacetic acid, methylamine, and ammonia. The relative positions of the methyl and phenyl groups follow from this. 4(or 5)-Nitroglyoxaline was methylated by treatment with methyl sulphate at 100° and yielded 63·4% of the theoretical of the 5-nitro to 0·24% of the 4-nitro compound. By nitration of 1-methylglyoxaline, 21% of the theoretical of the 4-nitro to 8% of the 5-nitro compound was obtained. 4-*Nitro*-1-*methylglyoxaline* has m. p. 133—134°; the *hydrochloride* yields the base when heated at 100°. 5-*Nitro*-1-*methylglyoxaline* has m. p. 55°; the *hydrochloride*, after drying at 100°, has m. p. 195° (effervescence); *picrate*, m. p. 153·5°. Reduction of 5-nitro-1-methylglyoxaline by stannous chloride gave methylamine, ammonia, and glycine ethyl ester as hydrochlorides. 4(or 5)-*Nitro*-1 : 3-*dimethylglyoxalinium iodide*, m. p. 181° (effervescence), was obtained by heating 5-nitro-1-methylglyoxaline with methyl iodide. By the action of methyl sulphate on 4-phenylglyoxaline in the cold and completion at 100°, a product was obtained from which (after the removal of unchanged material as nitrate) the 4-phenyl- and 5-phenyl-1-methylglyoxalines were separated as picrates (yields, 29·8 and

6·2% of the theoretical). 4-*Phenyl*-1-*methylglyoxaline* has m. p. 110—111°; the *hydrobromide* ($+1H_2O$) has m. p. 178—179°; *nitrate*, m. p. *ca.* 97°; *picrate*, m. p. 245°, microscopic needles. 5-*Phenyl*-1-*methylglyoxaline*, m. p. 96—97°, plates; *nitrate*, m. p. 176—177° (decomp.); *picrate*, m. p. 139°. 4(or 5)-*Phenyl*-1 : 3-*dimethylglyoxalinium iodide* forms colourless prisms, m. p. 147—148°. Nitration of 4-phenyl-1-methylglyoxaline took place on heating a solution of the nitrate in concentrated sulphuric acid at 100°. The chief product (56% of the theoretical yield) was 4-p-*nitrophenyl*-1-*methylglyoxaline*, pale yellow prisms, m. p. 195°. It forms a *nitrate*, cream-coloured, woolly needles, m. p. 197° (decomp.), and a *picrate*, m. p. 258°, microscopic needles. The nitrate of an isomeric base, presumably 4-o-*nitrophenyl*-1-*methylglyoxaline*, flat, colourless prisms, decomp. 182°, was formed in considerable amount and also a small amount of a dinitro derivative. 5-p-*Nitrophenyl*-1-*methylglyoxaline*, lemon-yellow needles, m. p. 171—172°, forms a *nitrate*, colourless plates, m. p. 213° (decomp.), and *picrate*, prismatic needles, m. p. 184°. Methylation of 4-*p*-nitrophenylglyoxaline gave 4-*p*-nitro- and 5-*p*-nitro-phenyl-1-methylglyoxalines in yields of 28 and 2·6% of the theoretical, respectively. 5-*Nitro*-4-p-*nitrophenyl*-1-*methylglyoxaline*, m. p. 208—209°, was made by warming the nitrate of the mononitro compound with concentrated sulphuric acid (*hydrochloride* described). 4-*Nitro*-5-p-*nitrophenyl*-1-*methylglyoxaline*, m. p. 187°, is similar in solubility to the 5-nitro compound. Methylation of 5-nitro-4-*p*-nitrophenylglyoxaline yielded 66% of crude methylated product, consisting mainly of 5-nitro-4-*p*-nitrophenyl-1-methylglyoxaline; none of the 4-nitro-5-*p*-compound could be isolated. Reduction of 5-nitro-4-*p*-nitrophenyl-1-methylglyoxaline by stannous chloride gave 68% of the theoretical yield of 5-*amino*-4-p-*aminophenyl*-1-*methylglyoxaline dihydrochloride*, which darkens above 200°. It is readily soluble in water. Aqueous solutions give a transient indigo colour with ammonia, reduce ammoniacal silver nitrate, and give a magenta solution with ferric chloride. On hydrolysis with concentrated hydrochloric acid at 170°, *p*-aminophenylaminoacetic acid dihydrochloride, ammonium chloride, and methylamine hydrochloride were obtained. A. C.

Synthesis of Heteroxanthine from an Iminazole [Glyoxaline] Derivative. J. SARASIN and E. WEGMANN (*Helv. Chim. Acta*, 1924, **7**, 713—719).—5-Chloro-1-methylglyoxaline [the 4-chloro-1-methylglyoxaline of Sarasin (A., 1923, i, 710, 711), the present investigation having shown that the names should be interchanged] is converted into the nitrate and this salt treated with concentrated sulphuric acid, whereupon 5-*chloro*-4-*nitro*-1-*methylglyoxaline*, m. p. 147—148°, is obtained. Reduction, or reduction followed by hydrolysis, of this substance gives abnormal results. When it is treated with potassium cyanide and a little potassium iodide in hot alcoholic solution, 4-*nitro*-5-*cyano*-1-*methylglyoxaline*, m. p. 141—142°, is obtained. This product is converted by the action of sulphuric acid into the *amide*, m. p. 257—258° (decomp.), of

4-*nitro*-1-*methylglyoxaline*-5-*carboxylic acid*, m. p. 160° (decomp.), the latter being obtained by alkaline hydrolysis of the amide, this being unaffected by boiling hydrochloric acid. At 120°, however, hydrolysis and decarboxylation take place, and 4-*nitro*-1-*methylglyoxaline*, m. p. 133—134°, is obtained. This is reduced by tin and hydrochloric acid, yielding a *hydrochloride*, presumably of 4-*amino*-1-*methylglyoxaline*, which, when heated with hydrochloric acid at 150°, is broken up into ammonia, a little methylamine, and sarcosine, identified as hydrochloride, m. p. 168—169°. The amide of 4-nitro-1-methylglyoxalinecarboxylic acid is reduced to the *amide*, m. p. 184—185°, of 4-*amino*-1-*methylglyoxalinecarboxylic acid*, the *hydrochloride* of the amide having m. p. 214—215°. This amino-amide reacts at 160—170° with ethyl carbonate to yield heteroxanthine (7-methylxanthine), m. p. 380° (decomp.), identical with the product obtained from theobromine.

4-Chloro-1-methylglyoxaline (*loc. cit.*) is also readily nitrated, yielding 4-*chloro*-5-*nitro*-1-*methylglyoxaline*, m. p. 77—78°. W. A. S.

Quaternary Salts of Iminazoles [Glyoxalines]. II. J. SARASIN and E. WEGMANN (*Helv. Chim. Acta*, 1924, **7**, 720—723; cf. A., 1923, i, 710, 711).—5-Chloro-2-methyl-1-ethylglyoxaline, the constitution of which follows from that of 5-chloro-1-methylglyoxaline (cf. preceding abstract), forms a *methiodide*, m. p. 202—203°, which, when heated in a vacuum at 240°, is broken up into ethyl iodide and 4-*chloro*-1 : 2-*dimethylglyoxaline*, m. p. 93—94°, b. p. 258—260° (*picrate*, m. p. 167—168°), which, when reduced with sodium and alcohol, affords 1 : 2-dimethylglyoxaline. Similarly, 5-*chloro*-2-*methyl*-1-*ethylglyoxaline ethiodide*, m. p. 142—143°, yields 4-*chloro*-2-*methyl*-1-*ethylglyoxaline*, b. p. 263—265° (*picrate*, m. p. 154—155°), which on reduction yields 2-methyl 1-ethylglyoxaline; the *propiodide*, m. p. 108—109°, affords 4-*chloro*-2-*methyl*-1-*propylglyoxaline*, b. p. 135—137°/12 mm. (*picrate*, m. p. 152—153°), and, thence, 2-*methyl*-1-*propylglyoxaline*, b. p. 222—223° (*picrate*, m. p. 142—143°); the iso*butiodide* affords 4-*chloro*-2-*methyl*-1-iso*butylglyoxaline*, b. p. 144—146°/12 mm. (*picrate*, m. p. 141—142°), and 2-*methyl*-1-iso*butylglyoxaline*, b. p. 225—226° (*picrate*, m. p. 151—152°); the iso*amiodide*, m. p. 133—134°, yields 4-*chloro*-2-*methyl*-1-iso*amylglyoxaline*, b. p. 153—155°/12 mm. (*picrate*, m. p. 120—121°), and 2-*methyl*-1-iso*amylglyoxaline*, b. p. 242—243° (*picrate*, m. p. 148—149°).

When the nitrate of 5-chloro-2-methyl-1-ethylglyoxaline is heated with sulphuric acid, 4-*nitro*-5-*chloro*-2-*methyl*-1-*ethylglyoxaline*, m. p. 88°, is obtained. 5-*Nitro*-4-*chloro*-2-*methyl*-1-*ethylglyoxaline*, m. p. 67°, is prepared in a similar way. W. A. S.

Compound of Antipyrine with Trichloroacetic Acid. L. DEBUCQUET (*J. Pharm. Chim.*, 1924, **30**, 121—122).—*Antipyrine trichloroacetate*, $C_{11}H_{12}ON_2,CCl_3{\cdot}CO_2H$, forms lustrous plates, m. p. 79—80°, and is dissociated in aqueous solution. W. T. K. B.

4-Dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone. CHEMISCHE FABRIK ALTSTETTEN AKTIEN-GES. (Swiss Pat. 99452; from *Chem. Zentr.*, 1924, i, 1272).—4-*Dimethylamino*-1-*phenyl*-

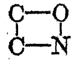
2 : 3-*dimethyl*-5-*pyrazolone* is prepared from 4-*sulphamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* by the action on it of formaldehyde in the presence of formic acid. G. W. R.

Synthesis of 1 : 2 : 4-Triazole Compounds. VIII. Benzoylformhydroxamic Acid and its Derivatives. C. GASTALDI (*Gazzetta*, 1924, **54**, 582—589).—As would be expected from the synthesis of 1 : 2 : 4-triazole compounds from the arylhydrazones of pyruvylhydroxamic acid (A., 1923, i, 1236), benzoylformhydroxamic acid, Bz·CO·NH·OH or OH·CBz:NOH, is converted quantitatively into benzamide and carbon dioxide when heated at its melting point, this reaction being apparently characteristic of free hydroxamic acids, having the grouping ·CO·CO·NH·OH or ·CO·C(OH):NOH; in the above instance, the formation of benzoylcarbimide as an intermediate compound was assumed, the reaction then proceeding thus: $NBz:C:O+H_2O \longrightarrow NHBz\cdot CO_2H \longrightarrow NH_2Bz+CO_2$ (cf. A., 1923, i, 1237).

Triazole compounds and benzamide may be obtained by heating at the melting point the acyl derivatives of the arylhydrazones of hydroxamic acids and benzoylformhydroxamic acid, respectively. In these cases, the reaction is determined by the temperature, and may be effected also by heating the acids in neutral solvents of high boiling point, such as naphthalene or α- or β-methylnaphthalene. If these solvents are replaced by aniline, the symmetrical disubstituted carbamides are formed, the intermediate formation of carbimides being thus proved: (1) $NPhMe\cdot N:CMe\cdot CO\cdot NH\cdot OAc+NH_2Ph \longrightarrow NPhMe\cdot N:CMe\cdot N:C:O+NHPhAc+H_2O \xrightarrow{+NH_2Ph} NPhMe\cdot N:CMe\cdot NH\cdot CO\cdot NHPh \xrightarrow{+NH_2Ph} NPhMe\cdot N:CMe\cdot NH_2+NHPh\cdot CO\cdot NHPh$. (2) $Ph\cdot CO\cdot CO\cdot NH\cdot OH \xrightarrow{-H_2O} Ph\cdot CO\cdot N:C:O \xrightarrow{+NH_2Ph} Ph\cdot CO\cdot NH\cdot CO\cdot NHPh$.

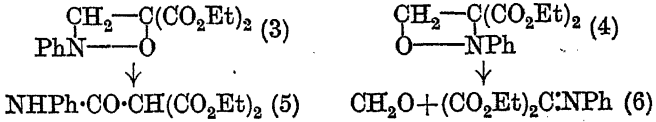
s.-Diphenylcarbamide is formed by the action of aniline on the acetyl derivative of pyruvylhydroxamic acid phenylmethylhydrazone (cf. A., 1923, i, 1237). s.-*Benzoylphenylcarbamide*, NHBz·CO·NHPh, has m. p. 207°. The *sodium* and *silver* salts of benzoylformhydroxamic acid are described. T. H. P.

Additive Formation of Four-membered Rings. V. Formation of Stable Dimethylene-1 : 2-oxaimines from Ethylenes and Nitroso Compounds, with Special Reference to the Direction of the Addition. C. K. INGOLD and S. D. WEAVER (*J. Chem. Soc.*, 1924, **125**, 1456—1462).—The compounds described are derivatives of the dimethyleneoxaimine ring:

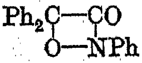
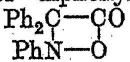
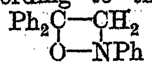
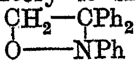


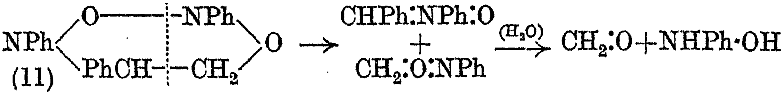
$\begin{matrix} C-O \\ | \quad | \\ C-N \end{matrix}$

(cf. this vol., i, 322, 323; also T., 1922, **121**, 2793; 1923, **123**, 2745), which have been produced by the additive union of unsaturated molecules —in the present case an ethylene derivative and a nitroso compound (C:C+N:O). To ensure the stability of this type of ring, it was found desirable to have a bulky *gem*-grouping attached to one of the ring-bound carbon atoms. The *gem*-substituted ethylenes, (1) $CH_2:C(CO_2Et)_2$ and (2) $CH_2:CPh_2$, were employed in the formation of these rings, which were found to be amongst the most stable four-membered heterocyclic rings yet produced. The direction of the addition of (1) or (2) with nitrosobenzene was found to be at variance with that required by the "theory of alternate polarities" (cf. Lowry, T., 1923, **123**, 822). Thus the ethylene derivative (1) combines readily with nitroso compounds to form rings of the type (3) and not (4), which should not be the case if oxygen key-atoms determine the polarities: $\mathrm{Ar{\cdot}\overset{+}{N}{:}\overset{-}{O}}$; $\mathrm{\overset{+}{C}H_2{:}\overset{-}{C}(\overset{+}{C}\overset{-}{O}_2Et)}$.



$$\begin{array}{ccc}\begin{array}{l}\mathrm{CH_2-C(CO_2Et)_2}\\ \mathrm{PhN-\!\!-O}\end{array}\ (3) & & \begin{array}{l}\mathrm{CH_2-C(CO_2Et)_2}\\ \mathrm{O-\!\!-NPh}\end{array}\ (4)\\ \downarrow & & \downarrow\\ \mathrm{NHPh{\cdot}CO{\cdot}CH(CO_2Et)_2}\ (5) & & \mathrm{CH_2O+(CO_2Et)_2C{:}NPh}\ (6)\end{array}$$

Ethyl 2-*phenyldimethylene*-1 : 2-*oxaimine*-4 : 4-*dicarboxylate* (3), colourless needles, m. p. 98—100°, was obtained when nitrosobenzene in chloroform was added to ethyl methylenemalonate. It exhibits no salt formation with either strong acids or alkalis; it gives no colour with ferric chloride, no copper salt, and is oxidised only with difficulty by alkaline permanganate. Its constitution is proved by the fact that it yields dicarbethoxyacetanilide (5) when heated at 100°, the identity of the latter being settled by a comparison with the condensation product of ethyl malonate and phenylcarbimide. On heating at higher temperatures (best 240—250°) 6-*anilino*-2 : 4-*diketo*-3-*phenyl*-2 : 4-*dihydro*-1 : 3-*oxazine*, m. p. 293—294°, is formed by the condensation of (5) with phenylcarbimide. *Ethyl* 2-p-*chlorophenyldimethylene*-1 : 2-*oxaimine*-4 : 4-*dicarboxylate*, m. p. 122—123°, and the corresponding p-*bromo* compound, m. p. 132—133°, were obtained similarly to (3) on using the *p*-halogen-substituted nitrosobenzenes. Staudinger and Jelagin (A., 1911, i, 215) obtained (7) and only traces of (8) by the addition of diphenylketen, $\mathrm{\overset{-}{O}\overset{+}{C}{:}\overset{-}{C}Ph_2}$, to nitrosobenzene,  $\begin{array}{l}\mathrm{Ph_2C-CO}\\ \mathrm{\ \ O-NPh}\end{array}$ (7),  $\begin{array}{l}\mathrm{Ph_2C-CO}\\ \mathrm{PhN-O}\end{array}$ (8), whilst (8) would be expected from the polarity theory. Diphenylethylene (2) is a compound in which the polarities are oppositely directed with respect to the heavy substituent to those of (1). It may be represented by the polar formula, $\mathrm{\overset{-}{C}H_2{:}\overset{+}{C}Ph_2}$. According to the polar theory it should unite with $\mathrm{O{:}\overset{+}{N}Ph}$ to form  $\begin{array}{l}\mathrm{Ph_2C-CH_2}\\ \mathrm{\ \ O-NPh}\end{array}$ (9) and not  $\begin{array}{l}\mathrm{CH_2-CPh_2}\\ \mathrm{O-\!\!-NPh}\end{array}$ (10). Only (10) was formed. 2 : 3 : 3-*Triphenyldimethylene*-1 : 2-*oxaimine* (10), m. p. 218—220°, closely resembled the above dimethyleneoxaimines. On distillation at 70 mm., it decomposed, yielding benzophenonanil and formaldehyde. As an example of an ethylene derivative in which the *gem*-group is absent, styrene was allowed to react with nitrosobenzene. No dimethyleneoxaimine was formed, the product being a six-membered ring (11) which breaks down into *N*-phenylbenzaldoxime, formaldehyde, and phenylhydroxylamine.



(11)

N-p-*Chlorophenylbenzaldoxime,* m. p. 172—173°, was obtained from styrene and *p*-chloronitrosobenzene. A. C.

Anhydrides of Amino-acids and their Derivatives. P. Karrer and C. Gränacher (*Helv. Chim. Acta,* 1924, 7, 763—780).—When 2 : 5-dihydroxydihydropyrazine dibenzyl ether (this vol., i, 212) and phthalic anhydride are heated together at 150—200°, glycine and benzylphthalic acid are formed, and when the pyrazine compound and methyl iodide are heated together at 100—120°, sarcosine anhydride and benzyl iodide are produced. The silver salt of glycine anhydride reacts with ethyl ω-chloro-*p*-toluate to give 2 : 5-*dihydroxydihydropyrazine di*-p-*carbethoxybenzyl ether,* m. p. 196—198°. The corresponding dicarboxylic *acid* melts and chars at 230—235°; it, like its congener (*loc. cit.*), is readily hydrolysed by dilute hydrochloric acid.

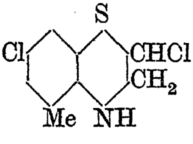
Ethyl hippurate is dehydrated when treated with phosphorus pentachloride (on the water-bath) yielding 5-*ethoxy*-2-*phenyloxazole,* b. p. 150—152°/12 mm. (*hydrochloride,* m. p. 115—120°; *picrate,* m. p. 122—123°). Warm, dilute hydrochloric acid readily decomposes this compound to ethyl alcohol and hippuric acid. Methyl acetamidoacetate, similarly dehydrated (in chloroform solution), yields 5-*ethoxy*-2-*methyloxazole,* b. p. 60—62°/10—12 mm. (*picrate,* m. p. 98°). The ethyl ester of benzoyl-*l*-leucine yields 5-*ethoxy*-2-*phenyl*-4-iso*butyloxazole,* b. p. 133—134°/2 mm. (*picrate,* m. p. 81°), and that of acetyl-leucine affords 5-*ethoxy*-2-*methyl*-4-iso*butyloxazole,* b. p. 87—89°/20 mm. (*picrate,* m. p. 80—81°). All these oxazoles are easily decomposed by dilute acid.

Hippuric anilide also is dehydrated by treatment with phosphorus pentachloride and thus affords 5-*chloro*-1 : 2-*diphenylglyoxaline,* m. p. 133° (*picrate,* m. p. 157—158°). The compound is stable towards hot hydrochloric acid; the chlorine atom also is firmly attached. 5-*Chloro*-2-*phenyl*-1-*ethylglyoxaline,* m. p. 65—67° (*picrate,* m. p. 160—161°), is obtained in a similar way from *hippuric ethylamide,* m. p. 147—148°. Hippuramide yields 5-*hydroxy*-2-*phenylglyoxaline,* m. p. 141—143°. This compound is decomposed by hot dilute hydrochloric acid.

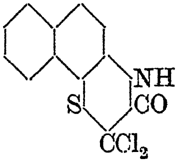
The relationship of the above investigations to the question of the structure of proteins is discussed. W. A. S.

Halogenated Ketodihydroaryl-*p*-thiazines. Farbwerke vorm. Meister, Lucius, & Brüning (K. Zahn) (D.R.-P. 379318; from *Chem. Zentr.,* 1924, i, 1104—1105).—The following compounds obtained by chlorination of ketodihydroaryl-*p*-thiazines in the methylene group of the thiazine ring are described: *Chloroketodihydrobenz*-p-*thiazine,* m. p. 212° (decomp.); *dichloroketodihydro-*

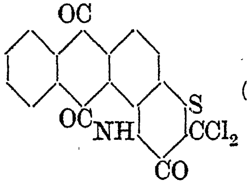
benz-p-*thiazine*, m. p. 185° (decomp.); *bromoketodihydrobenz*-p-*thiazine*; *dibromoketodihydrobenz*-p-*thiazine*; *chloroketodihydro-5-methyl-7-chlorobenz*-p-*thiazine* (I), m. p. 240°; *2-dichloroketodihydro-5-methyl-7-chlorobenz*-p-*thiazine*, m. p. 205°; *monochloroketodihydronaphth*-p-*thiazine*, blackening at 210°; *dichloroketodihydronaphth*-p-*thiazine* (II), m. p. about 230° (decomp.); *dichloroketodihydroanthraquinonyl*-p-*thiazine* (III).



(I.)



(II.)



(III.)

G. W. R.

4-Nitro-2-sulphophenyldehydrothio-*p*-toluidinesulphonic Acid. D. H. Peacock (*J. Chem. Soc.*, 1924, **125**, 1547).—This compound was prepared by condensing sodium dehydrothio-*p*-toluidinesulphonate with sodium 6-chloro-3-nitrobenzenesulphonate. The *potassium* salt, $C_{20}H_{13}O_8N_3S_3K_2$, dyes cotton in bright yellow shades tinged with green. The *silver*, *lead*, and *barium* salts have been prepared. The potassium salt with strong alcoholic potassium hydroxide yields a bronze, crystalline powder which appears to contain the :NK group.

4-*Amino-2-sulphophenyldehydrothio*-p-*toluidinesulphonic acid*, obtained on reducing the nitro compound, dyes cotton very pale shades. The diazo compound couples on the fibre with β-naphthol to produce a bright rose, and with *m*-phenylenediamine a full brown shade. A. C.

Condensation of Aryldiazonium Salts and of Alkyl Nitrites with Derivatives of Cyanoacetic Acid. T. K. Walker (*J. Chem. Soc.*, 1924, **125**, 1622—1625; cf. T., 1923, **123**, 2775).—Difficulties in preparing benzylcyanoacetic ester were overcome (yield 60%) by use of excess of cyanoacetic ester (cf. A., 1893, i, 16; 1899, i, 897), and treatment with sodium hydroxide gave the acid. Ice-cold solutions of alkylcyanoacetic acids reacted with aryldiazonium salts according to the equation $CHR(CO_2H)\cdot CN + Ar\cdot N_2\cdot OH \longrightarrow CR(:N\cdot NHAr)\cdot CN + H_2O$ (where $R = CH_2Ph$, Ph, or Et); the following hydrazones were thus obtained: *phenylpyruvonitrilephenylhydrazone* (100% yield), m. p. 157°, converted by boiling alcoholic potassium hydroxide into *phenylpyruvic acid phenylhydrazone*, m. p. 161°; *phenylpyruvonitrile*-p-*tolylhydrazone* (yield 25%), m. p. 113°; *phenylpyruvonitrile*-p-*nitrophenylhydrazone* (small yield), m. p. 167—168°; *methylpyruvonitrile*-p-*tolylhydrazone*, m. p. 143—144°; *methylpyruvonitrile*-p-*chlorophenylhydrazone*, m. p. 172°; *phenylglyoxylonitrilephenylhydrazone*, m. p. 152°.

Nitrous acid and alkyl nitrites were without action on monoalkylcyanoacetic acids, whilst the esters only yielded oximino derivatives, CN·CR:NOH, when treated with potassium ethoxide at 0° in dry ethereal solution. Thus ethyl benzylcyanoacetate reacted with amyl nitrite; cautious acidification yielded *phenylpyruvonitrile oxime*, an unstable red oil (*silver* salt described). Its constitution was established by hydrolysing with acid to hydroxylamine, whilst heating with alcoholic potassium hydroxide gave α-oximino-β-phenylpropionic acid. Similarly, from ethyl ethylcyanoacetate there was prepared *methylpyruvonitrile oxime*, a red oil (*potassium*, *sodium*, and *silver* salts described); ethyl phenylcyanoacetate gave *phenylglyoxylonitrile oxime* (small yield), m. p. 129°.

The general conclusion from these and previous results is that an aryldiazonium salt condenses with a compound CHRXY (where $X=CO_2H$, CO_2R', COR′, CN and $Y=CO_2H$, CO_2R'); alkyl nitrites condense similarly except when, simultaneously, X=CN and $Y=CO_2H$. Nitrosobenzene does not react with CHRXY, although it usually condenses readily with CH_2XY. F. M. H.

Preparation of Aminoazo Compounds. FARBENFABR. VORM. F. BAYER U. CO. (J. HALLER) (D.R.-P. 381916; from *Chem. Zentr.*, 1924, i, 1592).—Negatively substituted *o*-aminodialkylanilines are diazotised and the diazo compounds coupled with diazotisable amines. Compounds are thus prepared from diazotised 4-nitro-2-amino-1-dimethylaniline or 2-amino-4-methoxytoluene and *p*-xylidine, from diazotised 4-chloro-2-amino-1-dimethylaniline and 2-amino-4-methoxytoluene, and finally from diazotised 4-nitro-2-amino-*N*-methyldiphenylamine and *m*-aminoacetanilide. 4-*Nitro-2-amino*-N-*methyldiphenylamine* has m. p. 69—70°. G. W. R.

Halogen-substituted Aromatic Hydrazines. II. 2 : 3-, 2 : 5-, 2 : 6-, and 3 : 5-Dibromophenylhydrazines and *p*-Bromophenylmethylhydrazine and their Reaction Products with Aldehydes and Ketones. E. VOTOČEK and R. LUKES (*Bull. Soc. chim.*, 1924, [iv], 35, 868—879).—Of the above hydrazines, only the 2 : 5- and 3 : 5-dibromophenylhydrazines have been previously prepared. The 2 : 5-*dibromophenylhydrazones* of the following are described : *acetone*, m. p. 93°; *benzaldehyde*, m. p. 79°; *furfuraldehyde*, m. p. 104°; *arabinose*, m. p. 170—175°; *galactose*, m. p. 207°; *rhamnose*, m. p. 184°; *glucose* 2 : 5-*dibromophenylosazone*, m. p. 228—229°. The corresponding osazone of galactose could not be prepared in a pure state.

3 : 5-*Dibromophenylhydrazones* of the following are described : *acetone*, m. p. 85—86°; *benzaldehyde*, m. p. 106—107°; *furfuraldehyde*, m. p. 116°; *glucose*, m. p. 158—159°; *rhamnose*, m. p. 195—196°; *galactose*, m. p. 172°. The corresponding osazones of dextrose and galactose were isolated in an impure state.

2 : 3-*Dibromophenylhydrazine*, m. p. 112°, was prepared from 2 : 3-dibromoaniline by diazotisation and subsequent reduction with stannous chloride. *Acetone* 2 : 3-*dibromophenylhydrazone*, *benzaldehyde* 2 : 3-*dibromophenylhydrazone*, m. p. 106°, and the corresponding *osazones* of dextrose and galactose, which are both difficult to purify, are described.

2 : 6-*Dibromophenylhydrazine*, m. p. 110°, was similarly obtained

from 2 : 6-dibromoaniline. *Acetone* 2 : 6-*dibromophenylhydrazone* (oil), *benzaldehyde* 2 : 6-*dibromophenylhydrazone*, m. p. 51—52°, unstable, and *furfuraldehyde* 2 : 6-*dibromophenylhydrazone*, m. p. 62°, are described. This hydrazine forms no characteristic hydrazones or osazones with the sugars.

as.-p-*Bromophenylmethylhydrazine*, m. p. 33°, was obtained by bromination of phenylmethylhydrazine in cold concentrated hydrochloric acid solution. *Benzaldehyde* p-*bromophenylmethylhydrazone*, m. p. 106—107°, *acetone* p-*bromophenylmethylhydrazone*, an unstable oil, and *lævulose* p-*bromophenylmethylosazone*, m. p. 153°, are described.

It is proved by two methods that bromination of phenylmethylhydrazine under the above conditions leads to a *p*-bromo derivative. Methylation of *p*-bromoaniline followed by the formation and reduction of the corresponding nitrosoamine gives *p*-bromophenylmethylhydrazine identical with the compound produced by direct bromination of phenylmethylhydrazine. *p*-Bromophenylmethylhydrazine was also reduced to *p*-bromomethylaniline, giving a nitroso compound identical with that produced by the first method. In the bromination of phenylmethylhydrazine no *o*-bromophenylmethylhydrazine can be detected. A. E. C.

Formation of Triphenylmethylphosphinic Acid from Triphenylmethoxyphosphorus Dichloride. D. R. Boyd and F. J. Smith (*J. Chem. Soc.*, 1924, **125**, 1477—1480).—Alcoholic potassium hydroxide converts triphenylmethylphosphorus dichloride into an acid, which was assumed by Boyd and Chignell (T., 1923, **123**, 813) to have the formula $CPh_3{\cdot}O{\cdot}P(OH)_2$. Alkylphosphorous acids of this type are monobasic, but if the above acid dissolved in one equivalent of sodium hydroxide is titrated with more alkali, the curve showing the change of p_H with increase of alkali concentration indicates the presence of a second salt. The alternative formula, $CPh_3{\cdot}PO(OH)_2$, is more in harmony with the dibasic character of the acid. The latter forms triphenylmethane when heated with soda-lime, a reaction characteristic of phosphinic acids. There is evidently a molecular rearrangement during which tervalent phosphorus becomes quinquevalent. (1) $CPh_3{\cdot}O{\cdot}PCl_2 \longrightarrow CPh_3{\cdot}PO(OEt){\cdot}OK$.

In the case of the reaction between phosphorus trichloride and triphenylcarbinol, the reaction proceeds according to equation (2) to the extent of 78% of the carbinol employed (the normal reaction between phosphorus trichloride and an alcohol; Menschutkin, 1866) whilst about 5% of the carbinol appears to react according to (3): (2) $R{\cdot}OH+PCl_3=PHCl_3{\cdot}OR=PCl_2{\cdot}OR+HCl$. (3) $R{\cdot}OH+PCl_3=PHCl_3{\cdot}OR=PCl_2R{:}O+HCl$. Reaction (3) will tend to take place where the alcohol is pronouncedly basic with a tendency to dissociate into R· and ·OH. It is important to notice that $CPh_3{\cdot}O{\cdot}PCl_2$ is specially stable towards water whilst compounds of the type $R{\cdot}O{\cdot}PCl_2$ are usually readily hydrolysed by water. It is suggested that alcohol is first added on to the unsaturated phosphorus atom, then, under the influence of the hot alcoholic potassium hydroxide the disturbance of the molecule due to this and to the splitting off of hydrogen chloride may produce a state favourable to the migration of the triphenylmethyl group from oxygen to phosphorus as in (1) above. Directions are given for improving the yield of triphenylmethylphosphorus dichloride. Triphenylmethylphosphinic acid prepared as previously described was found to contain about 50% of its monoethyl ester; the pure acid has m. p. 275°. The yield was increased to 80% of theory by using 5—6 mols. of potassium hydroxide (in place of 3). *Dipotassium triphenylmethylphosphinate* (+$3H_2O$) and *barium triphenylmethylphosphinate*,

$$CPh_3{\cdot}PO_3Ba,4H_2O,$$

are described. A. C.

Chemistry of the Blood Colouring Matter. II. Chemical Character of Kathæmoglobin. F. Haurowitz (*Z. physiol. Chem.*, 1924, **137**, 62—77).—Mainly from spectroscopic and magnetic investigations of kathæmoglobin, the latter is shown to behave as if it were a Zsigmondy " colloid-compound " of hæmatin and globin. α-Hæmin (and from this, crystalline chlorohæmin) was obtained by digesting kathæmoglobin with pepsin and hydrochloric acid. B. F.

Products of the Catalytic Hydrolysis of Goose Feathers. W. S. Ssadikov and N. D. Zelinsky (*Biochem. Z.*, 1924, **147**, 30—69).—A highly detailed experimental account of the application to goose feathers of the authors' catalytic method of fragmenting proteins of which a preliminary announcement has already been made (A., 1923, i, 492). The isolation of many substances of the type of peptin and piprin anhydrides is described and the results of analyses are detailed. Such complex cyclic compounds are regarded as precursors of the amino-acids obtained on ultimate hydrolysis, the peptins giving rise to peptides as intermediates, and the piprins to piperidones. Many other complex derivatives, several of which are described, formed by secondary changes of the real protein units, may arise in the course of catalytic hydrolysis of ring structures. J. P.

Biochemistry.

Pharmacology of Cell Respiration. V. Influence of γ-Rays on Cell Respiration. F. Hazáma (*Z. physiol. Chem.*, 1924, **138**, 102—107).—Small doses of γ-rays usually cause a transitory increase in the oxygen consumption of the erythrocytes of the goose, provided that at least 4 hours have elapsed since the removal of the erythrocytes from the body; large doses are without effect. E. S.

Chondroitinsulphuric Acid in Serum. K. Dresel (*Klin. Woch.*, 1923, **2**, 2344—2345; from *Chem. Zentr.*, 1924, i, 1554—1555).—Chondroitinsulphuric acid, normally excreted in the urine, may be retained in certain pathological conditions. G. W. R.

Adsorption of Sodium Salicylate by Blood-serum. R. Coquoin (*Compt. rend. Soc. Biol.*, 1923, **89**, 1259—1261; from *Chem. Zentr.*, 1924, i, 1558).—On long-continued dialysis an equilibrium is established with respect to salicylate between serum and a physiological salt solution. No adsorption of sodium salicylate by serum takes place. This is contrary to the view of Chabanier, Lebert, and Lobo-Onell (*Compt. rend. Soc. Biol.*, 1923, **88**, 178). G. W. R.

Serum Proteins. (Method of Obtaining Serum and Criticism of Rohrer's Method of Determining the Albumin-Globulin Value.) W. von Frey (*Biochem. Z.*, 1924, **148**, 53—60).—The differences between plasma-serum and ordinary blood-serum (from a clot) are not evident if alterations of carbon dioxide tension are prevented by keeping the preparations under a layer of paraffin (cf. Leendertz, *Arch. klin. Med.*, 1922, **140**). Refractometric methods of determining serum proteins do not give trustworthy results, these being in general higher than those obtained by chemical methods. The Hammarsten and Rohrer methods of determining the albumin–globulin value do not give concordant results, a finding which is ascribed to the untrustworthiness of the latter method. J. P.

Effect of Exercise on Sugar and Residual Nitrogen in Blood. Cäsar and Schaal (*Z. klin. Med.*, 1924, **98**, 96—99; from *Chem. Zentr.*, 1924, i, 1553).—The blood-sugar was more than doubled after a foot race. The effect is reached 20—46 minutes after the event. No marked effect on the residual nitrogen of the blood was noted. G. W. R.

Changes in Blood-sugar. I. S. Nakahayashi and J. Abelin (*Biochem. Z.*, 1924, **147**, 544—556).—From determinations of the polarimetric and copper-reducing values (Bertrand) of deproteinised aqueous blood filtrates the authors claim to substantiate the results of Winter and Smith (*J. Physiol.*, 1922, **57**, 100). Although the figures published show a general tendency of the polarimeter value to rise, this is irregular and falls are sometimes recorded. In four normal cases (sheep's blood), the initial polarimeter value instead of being below the copper-reducing value, as the authors state, is above the latter or insignificantly below it. The feeding of thyroid material does not influence the behaviour of the blood filtrate, but after adrenaline injections this shows a polarimeter value above that of the copper-reducing value—exceptions again occur—and the general tendency is for the former to fall. Some days after the adrenaline injection the blood filtrates again show " normal " behaviour. J. P.

Distribution of Blood-sugar between Corpuscles and Plasma. F. HÖGLER and K. UEBERRACK (*Biochem. Z.*, 1924, **148**, 150—159).—In the rabbit, the ratio of corpuscle sugar to plasma sugar is very small. In human plasma, from blood to which anti-coagulant has been added in deficient amount, the blood-sugar results are too low. Hæmolysis leads to high results. Using sufficient anti-coagulant and avoiding hæmolysis, plasma and sera prepared by various methods give concordant blood-sugar results. Human corpuscles contain 50—80 mg. % of sugar. J. P.

Determination of Blood-sugar. L. PINCUSSEN and N. KLISSIUNIS (*Biochem. Z.*, 1924, **150**, 44—48).—Comparative determinations of blood-sugar from different parts of the circulation show that higher values may sometimes be obtained in blood from the right hand than in blood from the left, and in blood from either hand than in that from the lobe of the ear. It is suggested that blood obtained by capillary puncture (as from the ear) must always be diluted with tissue fluids; also that the blood is richer in sugar when circulating through active parts. The latter assumption is supported by the observation that the blood of a paralysed limb always contains less sugar than blood from other parts of the same individual's body. C. R. H.

Blood-sugar of Rabbits under Various Conditions. N. MOCHIZUKI (*Biochem. Z.*, 1924, **150**, 123—143).—Ligature of the pancreatic duct produces a gradually increasing degree of hyperglycæmia in rabbits; animals thus treated show a greater hyperglycæmia after feeding with dextrose and after injection of adrenaline than do normals; during the first 10 days after operation an increased proportion of the total blood-sugar is contained in the corpuscles. The slight rise in blood-sugar which follows administration of pilocarpine and of phloridzin in normal animals is replaced by a fall in the operated animals in the case of the latter substance, whilst in the case of the former no effect at all is observed. C. R. H.

Action of Uranyl Acetate. III. Action on Red Blood-corpuscles. III. Y. MIKAWA (*Biochem. Z.*, 1924, **149**, 550—555).—Uranyl acetate agglutinates the red corpuscles of rabbit blood without hæmolysing them. Such agglutinated corpuscles are not hæmolysed by saponin. This is probably due to a fixation of the hæmoglobin by the uranyl acetate. Small amounts of this salt damage the structure of the cells, as is shown by their increased sensitiveness to physiological saline solution. S. S. Z.

Partition of Chlorides between Plasma and Corpuscles in Human Blood. F. HÖGLER and K. UEBERRACK (*Biochem. Z.*, 1924, **150**, 18—22).—No difference could be detected between the chlorine content of serum and of plasma; the ratio of corpuscle-chlorine to plasma-chlorine is approximately constant both in normal individuals and in those suffering from nephritis, and is of the same magnitude as the ratio of the sugar of the corpuscles to the sugar of the plasma. C. R. H.

Changes in Chlorine Content of Whole Blood and Blood-serum of Infants in Relation to Gastric Secretion. W. SCHOBER (*Monatschr. Kinderheilk.*, 1923, **26**, 297—307; from *Chem. Zentr.*, 1924, i, 1948).—The chlorine content of the serum of suckling infants falls 2 hours after feeding, rising again after 3 hours. The chlorine content of the whole blood generally increases after feeding. The chlorine in the hydrochloric acid of gastric juice is not supplied entirely by the blood, but must come, in part, from chlorine reserves in the tissues. G. W. R.

Action of Intravenous Infusions of Sodium Chloride and Sugar on the Alkali Reserve of the Blood. Y. FUJIMAKI (*Arch. exp. Path. Pharm.*, 1924, **103**, 178—187).—One and a half hours after the injection of sodium chloride and sugar into the rabbit a rise in temperature is produced which is associated with diminished lung ventilation and a resulting retention of carbon dioxide. This is in turn compensated by an increase in the alkali reserve. J. P.

Acid–Base Equilibrium of the Blood of Normal Guinea Pigs, Rabbits, and Rats. J. A. HAWKINS (*J. Biol. Chem.*, 1924, **61**, 147—155).—Guinea pigs and rabbits, which show large variations in body temperature, show also variations in the acid–base equilibrium of their blood; rats, on the other hand, both in body temperature and in acid–base equilibrium, are relatively stable. C. R. H.

Effect of Methylamine Hydrochloride and Ammonium Chloride on the Physiological Osmotic Pressure of Sodium Chloride Solutions. M. DUVAL (*Compt. rend. Soc. Biol.*, 1923, **89**, 1268—1270; from *Chem. Zentr.*, 1924, i, 1558).—With rabbit blood-corpuscles methylamine hydrochloride and ammonium chloride behave like acetamide (Duval, *Compt. rend. Soc. Biol.*, 1923, **88**, 1196). In solutions poor in sodium chloride but rich in methylamine, hæmolysis occurs. Hæmolysis is due to the lowering of the physiological osmotic pressure of the solution against that of the blood-corpuscles. G. W. R.

Non-coagulable Nitrogen of Blood, and Muscular Work. G. AIELLO (*Rif. med.*, 1923, **39**, 721—722; from *Chem. Zentr.*, 1924, i, 1945).—Muscular work, involving protein decomposition and increase in blood concentration, resulted in an increase in the residual nitrogen of the blood. No relationship was observed between blood pressure and residual nitrogen. G. W. R.

Globulin and Albumin Coefficients of Serum especially during Pregnancy. H. KÜRTEN (*Arch. exp. Path. Pharm.*, 1924, **103**, 237—238).—A citation of the author's previous work (*Biochem. Z.*, 1922, **133**, 126; 1923, **135**, 536) in relation to that of Hafner (*Arch. exp. Path. Pharm.*, 1924, **101**, 336). J. P.

Investigations of the Blood of Individual Animals. III. W. KÜSTER (*Z. physiol. Chem.*, 1924, **138**, 21—37).—The preparation and alkylation of hæmins from the blood of different animals are recorded. The results indicate that the crude hæmin consists of a mixture and suggest that various hæmoglobins occur in one and the same blood. E. S.

Formation of Porphyrin from "Carbon Dioxide Blood." P. List (*Z. physiol. Chem.*, 1924, **138**, 164—170; cf. *ibid.*, 1924, **135**, 95).—From blood which has been saturated with carbon dioxide and subsequently treated with 25% hydrochloric acid there was obtained a substance of the nature of porphyrin which could be further separated into two components, one of which could be extracted from hydrochloric acid solution with chloroform whilst the other could not. Both components could be extracted together by means of ether after neutralising the solution and acidifying with acetic acid. Details are given of spectroscopic observations on the mixture and the two components separately. C. R. H.

Ammonia Content of Blood. V. Henriques and E. Gottlieb (*Z. physiol. Chem.*, 1924, **138**, 254—261).—A series of experiments on the amounts of ammonia recoverable from blood by prolonged aëration leads to the conclusion that the circulating blood contains no preformed ammonia, and that any which may be found is the product of *in vitro* reactions in the drawn blood. C. R. H.

Distribution of Carbamide in Blood and in Cerebrospinal Fluid. M. Polonovski and C. Auguste (*J. Physiol. pathol. gén.*, 1923, **21**, 267—282; from *Chem. Zentr.*, 1924, i, 1945—1946).—Plasma and serum have the same content of carbamide, but the erythrocytes contain 5 to 8% less. For every type of blood there is a characteristic distribution of carbamide, which is quickly restored if a part of the plasma is replaced by sodium chloride solution or by concentrated carbamide solution. Cerebrospinal fluid contains from 1 to 25% less carbamide than peripheral venous blood. G. W. R.

Fats and Lipoids in Blood. I. Distribution of Cholesterol and other Lipoids in the Blood of Different Animals. R. Iwatsuru (*Pflüger's Archiv*, 1924, **202**, 194—199; from *Chem. Zentr.*, 1924, i, 1947).—The cholesterol, fat, and lipoid content is practically constant in the corpuscles of various mammals. The values obtained were 215 mg. of cholesterol, and 580 mg. of fats and lipoids (calculated as triolein) per 100 c.c. of blood. Variations of these substances in the whole blood of various species and individuals are due to differences in the amounts appearing in the plasma. G. W. R.

New Basic Crystalline Constituent of Blood. I. A. Leimdörfer (*Biochem. Z.*, 1924, **149**, 513—524).—A new basic substance is described which can be obtained from the blood-corpuscles of human and mammalian blood by boiling with dilute acetic acid, extracting with alcohol, and precipitating with alcoholic cadmium chloride. It is present in the erythrocytes only. It gives a diazo reaction when sodium or potassium hydroxide is employed but not when ammonia or sodium carbonate is used. It is obtained from the cadmium compound by removing the metal with hydrogen sulphide, dissolving in alcohol, and precipitating with ether. It can also be precipitated directly from the alcoholic extract of the corpuscles with ether. The substance has not yet been prepared in a pure condition; the analyses suggest so far that it contains N, C, and H in the approximate proportions 1 : 3–5 : 7–9. S. S. Z.

Transformation of Blood Pigment into Bile Pigment. T. Brugsch and E. Pollak (*Biochem. Z.*, 1924, **147**, 253—254).—It is claimed that by the action of pyrocatechol, hæmin and its derivatives are converted into bile pigment (bilirubin). Quinol and resorcinol do not act in this way. J. P.

Blood Pigments. III. Methæmoglobin and its Derivatives. F. Haurowitz (*Z. physiol. Chem.*, 1924, **138**, 68—99).—Both colorimetric and spectroscopic methods show that methæmoglobin exists in two forms in aqueous solution. When the reaction of the medium is more alkaline than p_H 10·0 it is present entirely as alkaline methæmoglobin, and when more acid than p_H 6·0 entirely as acid methæmoglobin; between these hydrogen-ion concentrations equilibrium mixtures exist.

Pure, crystalline methæmoglobin is best prepared by allowing pure oxyhæmoglobin to stand for 6—8 weeks in 20% alcohol in the presence of air; its formation by means of other reagents has been studied. The action of nitrite on oxyhæmoglobin results in the formation of a mixture of nitric oxide–hæmoglobin and methæmoglobin and not, as stated by Hartridge (A., 1921, i, 135), of nitrite-hæmoglobin. Pure fluormethæmoglobin has been found to contain one atom of fluorine to one of iron. E. S.

Mechanism of Hæmolysis in Hypertonic Salt Solutions. D. Acél and L. Lorber (*Biochem. Z.*, 1924, **147**, 557—562).—Strongly hypertonic salt solutions (5—50%), except those with physiologically inactive anions (citrate, sulphate), hæmolyse red blood-corpuscles. The order of activity of the anions for salts with the same cation conforms to the Hofmeister series. In the salts of multivalent metals the activity of the cation is important. The process is regarded as being similar to hypotonic hæmolysis and support is thereby gained for the view that the erythrocyte is a colloidal structure containing hæmoglobin in its interstices, and not a closed semi-permeable membrane filled with the pigment. In weakly hypertonic solutions osmosis predominates, whilst in stronger salt solutions the imbibition of water by the colloid substance of the cells begins to play a part. J. P.

Influence of Sunlight on Protein Metabolism. L. Pincussen (*Biochem. Z.*, 1924, **150**, 36—43).—Irradiation causes an increase in the general metabolism of rabbits, as shown by an increase in nitrogenous excretion, which is increased by the use of sensitisers, such as various dyestuffs and potassium iodide. Differences in the action of the various sensitisers may be observed in their effect on individual constituents of the total excreted nitrogen. C. R. H.

Nitrogen Metabolism in Avitaminosis. S. Yoshiue (*Biochem. Z.*, 1924, **148**, 1—48).—In avitaminosed dogs, a diminution in intestinal absorption leads to a lessened urea formation and an increased excretion of amino-nitrogen and ammonia, a disturbance which can be reduced in intensity by any condition bringing about increased absorption. This condition of acidosis may appear at all stages of avitaminosis and is often apparently of a temporary nature and not directly associated with the latter, whilst at other times it is due to a progressive deterioration in the condition of the gastro-intestinal tract. An increase in protein metabolism, leading ultimately to a breakdown of cell proteins, is a primary result of avitaminosis. The rapidity with which the effects of avitaminosis become manifest is much greater in young than in old animals, varying more or less inversely with the age. J. P.

Pancreas and Carbohydrate Balance. E. Toenniessen (*Klin. Woch.*, 1924, **3**, 212—213; from *Chem. Zentr.*, 1924, i, 1557).—It is held that the pancreas does not take part in the catabolism of carbohydrates to lactic acid, but is concerned only in the later stages of degradation. G. W. R.

Lactic Acid Formation in Muscular Contraction. O. Meyerhof, H. E. Himwich, and Matsuoka (*Klin. Woch.*, 1924, **3**, 392—395; from *Chem. Zentr.*, 1924, i, 2174).—Contraction of isolated muscle caused by chloroform, caffeine, or heat is accompanied by the formation of lactic acid and is analogous in this respect to natural or electrically produced contraction. Contraction due to acetylcholine is not accompanied by lactic acid formation. Chloroform contraction can be inhibited by novocaine. G. W. R.

Muscular Exercise, Lactic Acid, and the Supply and Utilisation of Oxygen. I—III. A. V. Hill, C. H. N. Long, and H. Lupton (*Proc. Roy. Soc.*, 1924, **B**, **96**, 438—475).—I. *Introduction.* Previous work (A., 1923, ii, 977) and the various aspects of the problem as presented in skeletal and heart muscle, are discussed.

II. *Determination of lactic acid in biological fluids.*—Clausen's permanganate method (A., 1922, ii, 593) with slight modifications is considered suitable for blood and urine. In blood to which zinc lactate has been added about 85% of the lactic acid is found by this method. Resting human blood contains 10 to 20 mg.% and urine 3 to 14 mg.%. Oxidation with 50% sulphuric acid at 140° as described by Clausen (*loc. cit.*) does not give good results and even with 60% acid at 155° only 80% of the lactic acid is accounted for.

III. *Lactic acid in blood and the respiratory quotient.*—During steady, moderate exercise the variations in both respiratory quotient and total lactic acid of the blood are small. During and for a short time after severe exercise the lactic acid concentration increases to a maximum. The value then falls, owing to the diffusion of lactate ions into the blood stream and oxidative recovery. In blood to which lithium lactate has been added, the plasma attains a concentration of lactic acid about 50% higher than that of the blood as a whole, and in human blood after muscular exercise about 30% higher. The concentration in the corpuscles is considerably less than that in the plasma. The variations in the lactic acid concentration of muscle during exercise and in recovery lead to wide variations in the respiratory quotient. This increases with increase in vigour of the exercise and may reach the value of 2. It then falls to low values for a considerable period before returning finally to a normal resting value. All these changes depend merely on the liberation of lactic acid and its removal in recovery. O. O.

Degradation of Carbohydrates in Striped Muscle. IV. Biochemistry of α- and β-Glucose. F. Laquer and K. Griebel (*Z. physiol. Chem.*, 1924, **138**, 148—155).—The formation of lactic acid by a suspension of chopped muscle, already known (A., 1922, i, 1089; 1923, i, 268) to be increased by the addition of glycogen, is increased more by α-glucose than by β-glucose, the effect of ordinary dextrose being intermediate. In view of this it is suggested that α-glucose may be the particular form in which carbohydrate is actively metabolised in the organism. C. R. H.

Calcium Content of Normal and Diseased Skin. Gans (*Arch. Dermat. Syphilis*, 1924, **145**, 135—137; from *Chem. Zentr.*, 1924, i, 2162).—In normal skin, calcium occurs in the cutis, in rather less amount in the papillary bodies, with practically none in the epidermis. Changes in distribution occur in pathological conditions. In eczema, the calcium content of the epidermis greatly exceeds that of the papillary bodies and the cutis. A similar change is shown in the potassium content, principally on account of the exudative processes involved. G. W. R.

Retention of Lime by Animal Tissues. II. R. E. Liesegang (*Biochem. Z.*, 1924, **149**, 605).—Polemical. S. S. Z.

Calcium Fixation in the Development of Bone. E. Freudenberg and P. György (*Ergeb. inn. Med. Kindersheilk.*, 1923, **24**, 17—28; from *Chem. Zentr.*, 1924, i, 1952; cf. A., 1922, i, 608).—The physiological fixation of lime takes place in three stages which may be represented as follows: (1) cartilage protein + Ca=Ca–cartilage protein; (2) Ca–cartilage protein+phosphate= Ca–cartilage protein–phosphate; (3) Ca–cartilage protein–phosphate = calcium phosphate + cartilage protein. G. W. R.

Natural Porphyrins. VII. Urinoporphyrinogen Heptamethyl Ester and a New Conversion of Urino- into Coproporphyrin. H. Fischer and W. Zerweck (*Z. physiol. Chem.*, 1924, **137**, 242—264).—The two main porphyrins present in porphyrinuria, urino- and copro-porphyrin, have been separated by means of hot glacial acetic acid in which coproporphyrin is readily soluble whilst urinoporphyrin is practically insoluble. Further, by esterifying with methyl sulphate a new *porphyrin* has been isolated. The crystalline *methyl* ester has m. p. 255—257°. The new porphyrin forms a crystalline *copper* salt, m. p. 292°. On hydrogenating urinoporphyrin methyl ester in the presence of platinum, it takes up 4 atoms of hydrogen, and yields the leuco compound, $C_{47}H_{54}O_{16}N_4$ (colourless prisms, m. p. 148°). It is easily reconverted into urinoporphyrin by atmospheric oxidation. Urinoporphyrin, on oxidation with chromic acid, gives an inactive, crystalline carboxylated hæmatic acid. On reduction with hydriodic acid and phosphorus iodide, it yields a pyrrole acid giving an intense Ehrlich reaction. When the reduction is carried out in the cold ammonia is formed to the extent of one-third of the total pyrrole nitrogen. This is in harmony with the assumption that urinoporphyrin contains two hydroxypyrrole nuclei. The conversion of urinoporphyrin into coproporphyrin (A., 1916, i, 775) has been effected by heating it with 1% hydrochloric acid for 3 hours at 180—185°. D. R. N.

Natural Porphyrins. VIII. Occurrence of Urinoporphyrin (as Copper Salt, Turacin) in Turakoo Birds and the Demonstration of Coproporphyrin in Yeast. H. FISCHER and J. HILGER (*Z. physiol. Chem.*, 1924, **138**, 49—67).—The identity of turacin (A., 1923, i, 964) with the copper salt of urinoporphyrin has been confirmed by a comparison of the two salts; moreover, removal of the metal from turacin by reduction with sodium amalgam and subsequent oxidation in the air yields urinoporphyrin.

When the copper salts of coproporphyrin and urinoporphyrin are submitted to dry distillation, the products, which in each case consist of a new copper salt, have been shown by crystallographic and spectroscopic examination to be identical. That a relationship exists between coproporphyrin and urinoporphyrin is thus established.

Coproporphyrin, identified as its crystalline ester, has been isolated from putrefying yeast. This is the first occasion on which an animal porphyrin has been isolated from plant material. E. S.

Natural Porphyrins. IX. Ooporphyrin from Plovers' Egg Shells and its Relationship to Blood Pigments. H. FISCHER and F. KÖGL (*Z. physiol. Chem.*, 1924, **138**, 262—275).—The authors have isolated from plovers' egg shells a methyl ester which proves to be identical with the ooporphyrin dimethyl ester previously obtained from gulls' egg shells (this vol., i, 230). On boiling for 1 minute with a mixture of glacial acetic acid and hydriodic acid, this ester gives mesoporphyrin; with glacial acetic and hydrobromic acids it gives hæmatoporphyrin. These two reactions show that ooporphyrin belongs to the hæmoglobin group of pigments. The identity of ooporphyrin with Kämmerer's porphyrin and with the porphyrin obtained by Papendieck (this vol., i, 894) from blood treated with hydrogen sulphide, has been proved by the fact that the latter also undergo the two reactions mentioned above, and further by the identity of the complex salts with iron (" hæmin esters ") prepared from the dimethyl esters of all three porphyrins. C. R. H.

Natural Porphyrins. X. Blood Pigments in Yeast. Detection of Porphyrin in Plants. H. FISCHER and J. HILGER (*Z. physiol. Chem.*, 1924, **138**, 288—306).—In the autolysis of yeast there was obtained, besides the coproporphyrin already described (this vol., i, 894) as resulting from the bacterial putrefaction of yeast, Kämmerer's porphyrin, which was identified spectroscopically; after removing the porphyrin with 5% hydrochloric acid the solution of the remaining products of autolysis gave the hæmin spectrum, and on evaporation to dryness and treatment with pyridine, a definite hæmochromogen spectrum. The latter result was also obtained after plasmolysis of the yeast with ether and glacial acetic acid. Kämmerer's porphyrin was also obtained when blood was added to a fermenting mixture of sucrose and yeast, and after fermentation had ceased the whole was submitted to autolysis. Kämmerer's porphyrin was found in a sample of brewer's wort; coproporphyrin (probably) in hops. The spectra of porphyrins (unidentified) were obtained not only from grasses, by treating an alcoholic extract with glacial acetic acid, but also from chlorophyll-free coconut milk. C. R. H.

[Spectroscopic Chemical Reactions of Porphyrins and their Derivatives.] H. FISCHER (*Z. physiol. Chem.*, 1924, **138**, 307—313).—Polemical; reply to criticisms by Papendieck and Schumm (this vol., i, 460, 893) of the author's position with regard to the value of the spectroscopic method of analysis. C. R. H.

Compounds Extracted from Human Skeletal Muscle. Reply to J. A. Smorodinzev. R. ENGELAND and W. BIEHLER (*Z. physiol. Chem.*, 1924, **138**, 118).—Polemical (cf. this vol., i, 456). E. S.

Chemical Composition of Cardiac Muscle in Different Diseases. G. DOMAGK (*Z. klin. Med.*, 1924, **98**, 171—219; from *Chem. Zentr.*, 1924, i, 1551—1552).—Observations are recorded of the effect of certain pathological conditions on the content of non-protein nitrogen, fat, and water in cardiac muscle. G. W. R.

Metabolism of the Heart. I. Carbohydrate Balance of the Heart. P. SCHENK (*Pflüger's Archiv*, 1924, **202**, 315—328; from *Chem. Zentr.*, 1924, i, 2173).—The glycogen content of dogs' hearts is fairly constant. At any instant the content of carbohydrates intermediate between glycogen and lactic acid and including glucose and sugars of equal reducing power, forms a fairly constant proportion, approximately one-fifth, of the total carbohydrate present. The amount of lactic acid is extremely small and is probably due to the manipulations involved. It is improbable that lactic acid is a normal constituent of the resting muscle of warm-blooded animals. G. W. R.

Metabolism of the Heart. II. The Phosphoric Acid Balance of the Heart. P. SCHENK (*Pflüger's Archiv*, 1924, **202**, 329—336; from *Chem. Zentr.*, 1924, i, 2173; cf. preceding abstract).—The total phosphoric acid and lactacidogen phosphoric acid contents of heart muscle are appreciably higher than those of skeletal muscle. G. W. R.

Metabolism of the Heart. III. Carbohydrate and Phosphoric Acid Balance of the Heart after Injury. P. SCHENK (*Pflüger's Archiv*, 1924, **202**, 337—355; from *Chem. Zentr.*, 1924, i, 2173—2174; cf. preceding abstracts).—Data are given as to the effect of narcosis, hydrocyanic acid poisoning, and electrical stimulation on the carbohydrate and phosphoric acid balance in heart muscle. G. W. R.

Sulphuric Acid Content of Body Fluids in Normal and Pathological Conditions. R. MEYER-BISCH (*Biochem. Z.*, 1924, **150**, 23—35).—The concentration of total sulphuric acid in the blood-serum of normal individuals is about 18 mg. %. This amount is altered to a variable extent in nephritis and constantly raised in diabetes. The sulphuric acid content of the cerebrospinal fluid is greater than that of the serum, and is raised in meningitis, syphilis of the central nervous system, and encephalitis. Pleural exudates and œdema fluids contain about the same amount of sulphuric acid as the blood serum; lymph from the thoracic duct contains a variable amount but greater than the blood. C. R. H.

Solubility of Uric Acid. I. K. HARPUDER and H. ERBSEN (*Biochem. Z.*, 1924, **148**, 344—354).—In phosphate buffers uric acid is partly converted into urate, the amount of free uric acid in solution being independent of the hydrogen-ion concentration and practically constant about the true solubility value, whilst the proportion of urate depends on this constant concentration of free uric acid and on the hydrogen-ion concentration. The limiting degree of supersaturation of uric acid is partly dependent on the nature of the buffer acid present. J. P.

Solubility of Uric Acid. II. K. HARPUDER (*Biochem. Z.*, 1924, **148**, 355—369).—The behaviour of a supersaturated monourate solution at a p_H greater than 6·7 is ascribed to the presence of both undissociated uric acid and diurate, whilst in acid acetate and lactate buffers a supersaturation of undissociated uric acid is inferred. Non-electrolytes (dextrose, urea, glycine) and colloids (glycogen, globulin) increase the range of solubility of uric acid. J. P.

Groups Responsible for the Nucleal Coloration and Nucleal Reaction. R. FEULGEN and K. VOIT (*Z. physiol. Chem.*, 1924, **137**, 272—286).—Thymus-nucleic acid on mild partial hydrolysis gives rise to purines and substances which give an intense violet coloration with fuchsin–sulphurous acid and also the green pine-shaving reaction. The carbohydrate residue of thymus-nucleic acid is not a hexose, but a substance of unknown constitution. The nucleal reaction is not caused by furfuraldehyde, but is absolutely specific for (partly hydrolysed) thymus-nucleic acid. The substance which gives these reactions is very sensitive to acids, and on further hydrolysis ceases to give the colorations. It appears to be of the nature of thyminic acid (A., 1918, i, 413), which gives intense colorations with these tests (cf. this vol., i, 438). The isolation and determination of the nature of the carbohydrate residue in thymus-nucleic acid is rendered difficult as it readily decomposes, unlike the pentoses, under the influence of acids. The carbohydrate, like the furfuraldehyde derivatives (A., 1896, i, 144), gives the green pine-shaving reaction. This reaction is due to the presence of a free aldehyde grouping in thyminic acid, and is not given when the latter is oxidised or combined with another group, and therefore thymus-nucleic acid itself does not give this coloration. D. R. N.

Nature and Significance of the Lipoids of Protoplasm. W. Biedermann (*Pflüger's Archiv*, 1924, **202**, 223—258; from *Chem. Zentr.*, 1924, i, 2151).—Plant and animal protoplasms contain considerable quantities of lipoids, principally phosphatides of the lecithin type. They are probably held in adsorptive combination. Artificial digestion may be used to liberate them for analytical purposes. Lipoids exerting a protective effect against digestion occur not only in limiting membranes, but also within the protoplasm of plants. Animal protoplasm loses its resistance to digestion after death or injury. Plant protoplasm, however, retains this property so long as the lipoids are not extracted. G. W. R.

Molecular Stability of Acetic-choleic Acid. C. T. Mörner (*Z. physiol. Chem.*, 1924, **138**, 177—183).—Two samples of acetic-choleic acid were kept for a prolonged period in desiccators, one over sulphuric acid, and the other over sulphuric acid and quicklime. In both there were observed (1) a continuous decrease in weight, (2) at first a fall and then a rise in the melting point. The molecular weight increased in the course of the experiment (306 days) from 226 to 353. These changes indicate a continuous decomposition with loss of acetic acid, and the result is in contradiction to the claim of Wieland and Sorge (A., 1916, i, 710) regarding the extreme stability of acetic-choleic acid. C. R. H.

Fugutoxin. F. Ishiwara (*Arch. exp. Path. Pharm.*, 1924, **103**, 209—222).—Pure fugutoxin from the ovary of *Spheroides* melts at 120°, has $[\alpha]_D^{0}$ +17° to +27°, and exhibits chemical properties which suggest that it is a glucose ester and not a glucoside. It yields an osazone of m. p. 207·5°. J. P.

Spermine. III. F. Wrede (*Z. physiol. Chem.*, 1924, **138**, 119—135; cf. this vol., i, 77, 78).—From human semen the author has isolated the *chloroaurate* of a base which proves to be identical with the spermine described by Schreiner (A., 1879, 72). This salt crystallises in leaflets which darken at 210° and melt at 216—218° (decomp.). The *chloroplatinate* forms orange plates which darken at 235° and melt at 242°. The *picrate* sublimes at 200° and melts at 240° (decomp.); the *picrolonate* sublimes at 240° and decomposes at 280°. The *m*-nitrobenzoyl derivative has m. p. 171°. Molecular-weight determinations on the *m*-nitrobenzoyl derivative give values about 800, whence the formula of the base becomes $C_{10}H_{26}N_4$. C. R. H.

Lignoceric Acid. P. A. Levene, F. A. Taylor, and H. L. Haller (*J. Biol. Chem.*, 1924, **61**, 157—161).—The earlier conclusions (A., 1913, i, 1151; 1914, i, 1123) that lignoceric acid differs in constitution from *n*-tetracosanic acid, subsequently criticised by Brigl and Fuchs (A., 1922, i, 712), are now confirmed by the preparation from distinct sources of two samples of the acid, which, separately and when mixed, melted at 80·5—81°, both before and after the fractional crystallisation described by Brigl and Fuchs.
C. R. H.

Egg of *Bombyx Mori*—Proteins, Reactions. L. Pigorini (*Arch. Farm. sper. Sci. aff.*, 1924, **37**, 221—230).—The eggs of the silkworm appear to contain (1) albumins, (2) globulins, (3) vitellins and nucleo-proteins, and (4) a substance allied to the ovomucoid of birds' eggs. During incubation of the eggs, the compounds of group (1) remain practically constant in amount until two days before hatching and then diminish considerably, those of groups (2) and (4) decrease slightly throughout the whole period of incubation and to a greater extent during the last two days, and those of group (3) increase continuously during the incubation; apparently the last compounds are those which are utilised principally in the formation of cytoplasm in the embryo. Except during the last two days of the incubating period, the ratio of the amount of albumins to that of globulins in the egg has the approximate value 1 : 0·7. The acidity of the alcoholic extract of the eggs, calculated as grams of oxalic acid per 100 g. of the eggs, increases from 4·536 before incubation to 5·166 at the seventh to ninth day and then falls to 2·709 at the end of the incubation on the twentieth day.
T. H. P.

Imitation of Nervous and Cellular Tissue by means of Potassium Hydroxide, Silica, and Alcohol. L. A. Herrera (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 510—512).—A solution of 1 g. of potassium hydroxide and 1 g. of lactose in 50 g. of absolute alcohol dissolves the silica gel prepared by adding alcohol to potassium silicate. When such solutions are suitably dried, almost exact imitations of nervous and cellular tissues are obtained.
T. H. P.

Precipitation of the Casein of Human Milk. F. Demuth (*Biochem. Z.*, 1924, **150**, 144—148).—In the presence of suitable buffer mixtures the precipitation of the casein of human milk can be brought about constantly and rapidly, the optimum p_H being about 4·5. C. R. H.

Presence of a Hitherto Undescribed form of Urea in Human Urine. W. O. Moor (*Biochem. Z.*, 1924, **149**, 575—584).—In preparing urea from human urine a non-crystalline residue is obtained which consists of two substances, namely a crystalline urea and another non-crystalline substance isomeric with urea. This residue is soluble in water, in absolute alcohol, and in methyl and amyl alcohols, but is insoluble in ether and in chloroform. It contains a basic and an acidic substance. The former combines with oxalic acid, the latter with barium oxide. The barium salt of the acid substance contains nitrogen and sulphur. On shaking the residue with charcoal, the acid substance is adsorbed, whilst the other substance is converted into ordinary crystalline urea. The blue reaction given by urine with ammonia and phosphotungstic acid is due to the presence of the above residue. S. S. Z.

Ionic Acidity in Normal Human Urine. Influence of Food. P. Le Noir and A. M. de Fossey (*Compt. rend.*, 1924, **178**, 2008—2010).—The hydrogen-ion concentration of the urine of a normal person varies as a result of ingestion of food. During a meal, gastric secretion is accompanied by a decrease in urinary acidity in all cases where a normal mixed diet is taken. This phase is succeeded by increase of acidity, the extent and duration of which vary with different subjects and are not constant even in the same individual. H. J. E.

Effect of Phosphoric Acid on Excretion of Chlorine. W. Röckemann (*Arch. Kinderheilk.*, **72**, 161—171; from *Chem. Zentr.*, 1924, i, 1405).—The excretion of chlorine in urine and fæces is diminished after administration of sodium dihydrogen phosphate. G. W. R.

Uric Acid Excretion in the Dog. L. Rosenfeld (*Z. physiol. Chem.*, 1924, **138**, 276—279).—The oral administration of 15 g. and 7·5 g. of uric acid on two separate occasions led to approximately the same (small) increase in excretion of uric acid and total nitrogen, which bears no relation to the amount of uric acid ingested. C. R. H.

Influence of Guanylic and Adenylic Acids on Uric Acid Excretion. L. Rosenfeld (*Z. physiol. Chem.*, 1924, **138**, 280—287).—Intravenous administration of the sodium salts of guanylic and adenylic acids to dogs and rabbits led to a smaller increase in uric acid excretion and a larger increase in total nitrogen excretion than could be accounted for theoretically by the amount of substance injected. C. R. H.

Effect of Salts of the Rare Earths on the Excretion of Uric Acid. Pompeani (*Compt. rend. Soc. Biol.*, 1924, **90**, 2—4; from *Chem. Zentr.*, 1924, i, 1557).—Salts of thorium, cæsium, and didymium, subcutaneously administered, were without effect on the excretion of uric acid. Some effect was observed with salts of samarium and yttrium. G. W. R.

Creatinine Content of the Urine of Healthy and Sick Children. A. Lorenzini (*Bull. Sci. Med.*, 1922, **10**, 245—264; from *Chem. Zentr.*, 1924, i, 1555).—The creatinine content of the urine is generally smaller in children than in adults. Data are given for the influence of certain diseases on the amounts of creatine and creatinine found in the urine. G. W. R.

Creatinine Excretion of Various Domestic Mammals. J. Szende (*Biochem. Z.*, 1924, **149**, 566—571).—The following are the average figures for the creatinine content of 1000 c. of urine: dog 1·87 g., cat 1·76 g., cattle (stall) 3·98 g., cattle (after killing in slaughter-house) 9·41 g., horse 3·59 g. Paralytic hæmoglobinæmia and tetanus raise considerably the creatine content of horse's urine. S. S. Z.

Urinary Pigment in Normal and Pathological Conditions. H. Fischer and W. Zerweck (*Z. physiol. Chem.*, 1924, **137**, 176—241).—Urochrome can be prepared in quantity by concentrating in vacuum to a syrup large volumes of normal urine. The crystalline mass is filtered off and the syrupy mother-liquor containing most of the pigment submitted to dialysis. The pigment, which is not dialysable, is then isolated from the dialysed solution by acidification, when it is obtained in amorphous flocks. Analysis gave C=52%, H=6%, N=11%, and S=2% (cf. A., 1907, i, 993; 1909, i, 920; 1923, i, 417). It is sparingly soluble in water and most organic solvents. On hydrolysis with hydrochloric acid, it yields tyrosine, leucine, histidine, and arginine. Contrary to previous observations, pyrrole does not appear to be present in the pigment and also Ehrlich's aldehyde reaction in both acid and basic fractions of the hydrolytic products was negative. Trypsin had no effect on the pigment. The amino-nitrogen content of the pigment according to Van Slyke's method amounted to 10% of the total nitrogen. The conclusion is drawn from these results that the colouring matter is definitely a protein derivative. A brown pigment from a case of porphyrinuria was also isolated. It differs from the pigment in normal urine in that it is readily adsorbed on aluminium hydroxide, from which it can be removed by means of ammonia, and precipitated from the ammoniacal solution by acidification as in the case of the normal pigment. Its elementary composition and the examination of its products of hydrolysis suggest that the two are very closely related. The content of the brown pigment is always dependent on the porphyrin content of the urine and the two vary together. It is believed that both pigments are derived from a chromoprotein present in muscle, the porphyrin originating from its prosthetic constituent and the brown pigment from the protein moiety. D. R. N.

Conversion of Urobilinogen into Urobilin. S. Biro (*Biochem. Z.*, 1924, **149**, 459—467).—Urobilin cannot be detected in freshly collected urine containing urobilinogen. The latter becomes gradually converted into urobilin both in the presence and in the absence of light. This conversion takes place also when Ehrlich's reagent is added to the urine, and can be followed spectroscopically. S. S. Z.

Volatile Fatty Acids in Fæces. A. Cecchini (*Arch. patol. clin. med.*, 1923, **2**, 361—392; from *Chem. Zentr.*, 1924, i, 2166—2167).—Volatile fatty acids in fæces are not necessarily derived from fats and carbohydrates, but can arise from the bacterial decomposition of amino-acids. They are generally present in inverse relationship to indican in the urine. Acetic and butyric acids are commonly present but formic acid is never found. Saline aperients do not alter the bacterial flora of the intestine. From the occurrence, in certain cases, of butyric acid in urine, it is concluded that resorption of the toxic products of intestinal fermentation can take place. G. W. R.

Elimination of Methyl Alcohol and the Conditions for its Accumulation. E. M. P. Widmark and N. V. Bildsten (*Biochem. Z.*, 1924, **148**, 325—335).—The rabbit excretes methyl alcohol in constant amount in unit time independently of the concentration in the blood in such a way that the amount present in the latter, y, at a time, t, after the injection is expressed by the equation $y = (b - \beta)t$, where b is the amount administered and β the amount eliminated. The conditions for the accumulation of the alcohol in man are discussed. J. P.

Content of Calcium and Magnesium in Cancerous Blood. L. Blum and A. Klotz (*Compt. rend. Soc. Biol.*, 1923, **89**, 1335—1336; from *Chem. Zentr.*, 1914, i, 1553).—In the majority of cases cancer had no effect on the calcium and magnesium content of blood. G. W. R.

Composition of Blood in Epilepsy. G. Pezzali (*Rif. med.*, 1923, **39**, 433—437; from *Chem. Zentr.*, 1924, i, 929).—In epileptic blood there is no marked change in residual nitrogen, sugar, and chlorine. A definite decrease in cholesterol and fat, succeeded by a slight increase, and a marked increase in calcium and, frequently, of indican occur during the attack. G. W. R.

Deficiency of Calcium Ions in the Blood of Epileptics. E. J. Bigwood (*Compt. rend. Soc. Biol.*, 1924, **90**, 98—100; from *Chem. Zentr.*, 1924, i, 1947; cf. this vol., i, 680).—The relationship between p_{H} and p_{Ca} is not affected by epilepsy. After administration of sodium borotartrate alkalosis persisted whilst p_{Ca} remained within physiological limits. In such cases, convulsions do not occur. They are associated more with calcium shortage than with alkalosis. Similar conditions obtain in tetany. G. W. R.

The Amount of Calcium in the Blood and of Amino-acids in the Serum in Cases of Struma and Myositis Ossificans. A. Szenes (*Mitt. Grenzgeb. Med. Chirurg.*, 1923, **36**, 591—605; from *Chem. Zentr.*, 1924, i, 2164—2165).—The effect of different types of struma on the calcium content of the total blood and the refractive index of the serum is described. In general, the former is above normal and the latter lower with large than with small tumours and highest with malign tumours. The amino-acid content of the serum was above normal in two cases of large tumours, In a case of myositis ossificans a high calcium content in the blood was observed. G. W. R.

Significance of Ions in Muscle Function. III. Influence of Various Cations on the Chemical Activity of Striated Frog Muscle. H. Lange (*Z. physiol. Chem.*, 1924, **137**, 105—153).—Muscular contraction is accompanied by a series of changes of chemical and colloidal nature. Lactacidogen is converted by enzymic decomposition into free phosphoric and lactic acids which further bring about physical transformations in the muscle fibre and the covering membrane. This dissimilatory phase is followed by a rapid re-synthesis of the active substance. The chemical transformations in the muscle fibre for the time being control the absorptive condition of the sarcoplasm, and similar processes in the latter regulate the lactacidogen metabolism in the fibre. The cations may be divided into two groups according to their influence on the lactacidogen metabolism in fresh muscle. The first group, which displaces the enzyme equilibrium towards the synthetic side, comprises calcium, barium, and strontium and the second group, which does not possess this property or exhibits a contrary effect, comprises sodium, potassium, ammonium, and magnesium. The action of calcium at different concentrations varies remarkably, promoting synthesis strongly at some, and at others even showing a feeble contrary effect. On the other hand, magnesium, potassium, and sodium, especially at higher concentrations, inhibit the decomposition of lactacidogen, whilst potassium even promotes its synthesis. Calcium ions behave differently from other ions ($Na^{\cdot}$, $K^{\cdot}$, and $Mg^{\cdot\cdot}$) in inhibiting the formation of lactic acid. Calcium ions strongly accelerate the decomposition of glycogen, and sodium, potassium, and magnesium ions act similarly, although to a much smaller extent. Calcium ions inhibit strongly oxidative processes, whilst potassium chloride behaves differently in producing at first a very rapid transitory increase in respiratory activity. The action of all these ions is controlled very largely by the hydrogen-ion concentration. The action of salts is due to their influence on the colloidal conditions of the tissue as well as to their effect on the enzymes. D. R. N.

Significance of Ions in Muscle Function. IV. Enzymic Synthesis of Lactacidogen under the Influence of Ions. G. Embden and C. Haymann (*Z. physiol. Chem.*, 1924, **137**, 154—175).—The course of lactacidogen metabolism in the press juice of frog's muscle is influenced strongly by the addition of inorganic salts, both by the anions as well as the cations; CNS′, I′, and Cl′ accelerate the degradation of lactacidogen, whilst fluorine, citrate, and calcium ions induce strongly the synthesis of lactacidogen. Thus lactacidogen synthesis under the influence of fluorine ions can be easily followed by the almost complete disappearance of inorganic phosphoric acid and by the isolation of its characteristic osazone. By the simultaneous addition of glycogen the lactacidogen synthesis is so strongly favoured that inorganic phosphoric acid, even when present in minute amounts, disappears; dextrose and maltose have no such influence. The maximum amount of synthesis of lactacidogen under the influence of fluorine ions is obtained within the first few hours and thereafter the inorganic phosphoric acid content again gradually increases. D. R. N.

Diffusion of Glucose in the Organism. A. Chauffard, P. Brodin, P. Zizine, and A. Grigaut (*Compt. rend. Soc. Biol.*, 1923, **88**, 1022—1024; from *Chem. Zentr.*, 1924, i, 1408).—The diffusibility of glucose through animal membranes is considerably less than that of sodium chloride, sodium urate, and carbamide, respectively. The content of different physiological fluids in diffusible substances is compared. G. W. R.

Electrolytes of High Molecular Weight and their Significance in the Cell. H. Hammarsten (*Biochem. Z.*, 1924, **147**, 481—543).—Pure disodium guanylate was prepared by hydrolysis of sodium (yeast) nucleinate ("Astra") in an autoclave with 5% sodium hydroxide for 30 minutes at 100° in the presence of sodium acetate. Disodium guanylate was completely precipitated at 0° by the addition of acetic acid, and was further purified by Feulgen's method. From the disodium salt guanylic acid was obtained by precipitation as the copper salt and treatment of the latter with hydrogen sulphide. The partly precipitated acid was separated from copper sulphide by means of barium hydroxide solution and was finally liberated from the barium salt by sulphuric acid. Guanylic acid has a dissociation constant of $4{\cdot}45 \times 10^{-3}$. Disodium guanylate dissociates as does a normal inorganic bivalent salt, and the migration velocity of the bivalent guanylate ion at 20° is 48·3. The free acid and its sodium salt have osmotic pressures which agree with the Arrhenius–van't Hoff theory, and that of the salt is lowered by sodium and magnesium chlorides, more especially by the latter. Guanylic acid only shows typical amphoteric behaviour in strongly acid solutions or when present in large excess. Strongly basic amino-acids or proteins (lysine, histone chloride) form salt-like combinations with guanylic acid which are readily split up by dialysis in the presence of neutral salts. Glycocholic acid has $k=4{\cdot}0 \times 10^{-5}$, whilst taurocholic acid is a much stronger acid. Extending these investigations to histone and protamine chlorides, and to the sodium and alkylammonium salts of glycocholic, taurocholic, and thymus-nucleic acids and of Congo-red and related dyestuffs, it is concluded that in such electrolytes of high molecular weight, osmotic pressure is dependent not only on the degree of dissociation, but also on the molecular volume of the substance, and is often less than the Arrhenius–van't Hoff and Bjerrum–Debye theories demand. The amount of this abnormality in osmotic pressure is a function of the ratio of the ionic volume of the larger ion to that of the smaller—if the latter is increased the osmotic pressure rises. Importance is attached to such osmotic studies in relation to the biochemistry of the living cell. J. P.

Effect of Phosphates in (Magnesium) Narcosis. K. Spiro (*Klin. Woch.*, 1923, **2**, 2039; from *Chem. Zentr.*, 1924, i, 1410).—Injection of phosphates neutralises magnesium narcosis. G. W. R.

Effect of Veratrine on the Intestines and the Uterus and Importance of Potassium and Calcium Ions in this Connexion. E. L. Backman (*Compt. rend. Soc. Biol.*, 1924, **90**, 128—131; from *Chem. Zentr.*, 1924, i, 1560—1561).—Veratrine raises the tone of the musculature of the surviving intestine and uterus of rabbits and guinea pigs. Calcium in small doses strengthens this action whilst in large doses it acts in the opposite sense. Potassium also antagonises the effect of veratrine. G. W. R.

Action of *p*-Dihydroxycamphane (Bredt). H. Leo (*Arch. exp. Path. Pharm.*, 1924, **103**, 135—137).—The increased action on the heart and on respiration of *p*-hydroxycamphor as compared with camphor and diketocamphane is not shown on introducing a second hydroxyl group, as in *p*-dihydroxycamphane, but is, on the contrary, abolished, and this new compound exhibits, indeed, a strong paralysing effect. J. P.

Diuretic and Antidiuretic Effects of Pituitary Extract. W. G. Mackersie (*J. Pharm. Exp. Ther.*, 1924, **24**, 83—99).—It is suggested that the effect of pituitary extract on the rate of urinary secretion may be of use as a supplement to the uterine test for this substance, since such substances as histamine and ergotóxin, the presence of which may lead to confusion in the uterine test, have no effect on the secretion of urine. C. R. H.

Increased Absorption of Cholesterol in the Presence of Deoxycholic Acid. R. Schönheimer (*Biochem. Z.*, 1924, **147**, 258—263).—The administration to rabbits and guinea-pigs of sodium deoxycholate along with fat produces a marked increase in the rate of absorption of the latter and a pronounced lipæmia. Rabbits on a cholesterol–fat diet to which the bile salt is added show a marked increase in serum cholesterol, which is not evident if no sodium deoxycholate, or if it alone, is given. J. P.

Chemistry and Pharmacology of Kawa-kawa (*Piper methysticum*. K. Schübel (*Arch. exp. Path. Pharm.*, 1924, **102**, 250—282).—Kawa resin has a weak narcotic action, paralyses sensory nerves, and first stimulates and then paralyses smooth muscle. The hydrolysis products of the resin show similar actions. The local anæsthetic action is ascribed to compounds of the benzoic and cinnamic acid group. Kawa root contains no glucosides, nor were alkaloids detected in the resin, although nitrogen is present. From the hydrolysis products of the resin was isolated kawaic acid, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$, yellow needles or plates from benzene, m. p. 165° (decomp.) (cf. Borsche and Roth, A., 1921, ii, 862). The ethyl ester, tasting of pepper, was prepared. Kawaic acid produces an increased reflex excitability and a diminished blood pressure. By vacuum distillation of the residue from the crystallisation of kawaic acid were obtained (1) a pale yellow oil containing nitrogen and tasting of pepper, which possessed a weak narcotic action, and stimulated the digestive glands, and (2) a crystalline, unsaturated acid, m. p. 51—53°, with no narcotic action. J. P.

Mechanism of Catalytic Action of Iron Salts. I. O. Baudisch and L. A. Welo (*J. Biol. Chem.*, 1924, **61**, 261—274).—A review of previously published work by the author and others on the catalysis of oxidations and reductions by iron salts.
C. R. H.

β-Oxidation in the Kidneys. I. Snapper and A. Grünbaum (*Biochem. Z.*, 1924, **150**, 12—17).—After perfusion of the isolated kidneys of various animals with blood to which had been added phenylacetic acid or phenylbutyric acid there was obtained in the perfusion fluid phenylaceturic acid, whereas the perfusion of phenylpropionic acid or phenylvaleric acid led to the formation of hippuric acid, thus showing that β-oxidation (Knoop, A., 1905, ii, 46) can take place in this organ.
C. R. H.

Copper, Enzymes, and Fertilisation. O. Glaser (*Biol. Bull. Marine Biol. Lab.*, 1923, **44**, 79—104; from *Chem. Zentr.*, 1924, i, 2281—2282).—Eggs of *Arbacia* absorb copper ions from sea-water to which copper sulphate is added. Copper is also a normal constituent of *Arbacia* eggs and increases in amount up to maturity. After fertilisation the copper content decreases probably owing to secretion of pigment.
G. W. R.

Hydrolysis of Nucleic Acid by Takadiastase. J. Noguchi (*Biochem. Z.*, 1924, **147**, 255—257).—Takadiastase contains nucleinase and nucleotidase, capable of hydrolysing yeast and thymus-nucleic acids with the liberation of phosphoric acid and purine bases.
J. P.

Effect of α- and β-Methylglucosides on Taka-invertase. Y. Hattori (*Biochem. Z.*, 1924, **150**, 150—158).—The hydrolysis of sucrose by the invertase of takadiastase is inhibited by β-methylglucoside and unaffected by α-methylglucoside, whereas the reverse is true of yeast invertase. The type of inhibition, as shown by the time relations of the reaction, resembles that brought about by lævulose.
C. R. H.

Participation of Co-zymase in the Degradation of Sugar. K. Myrbäck and H. von Euler (*Ber.*, 1924, **57**, [*B*], 1073—1076).—The co-enzyme content of a bottom yeast was diminished by about 55% by desiccation under the conditions usual in practice, but remained almost unchanged when the specimen was rapidly spread in a thin layer on porous clay. The presence of co-zymase was established in a *Torula* from kefir, which produces alcohol, in a product from the same source which ferments lactose, yielding unknown substances, and in *Streptococcus lactis*. Its presence could not be established in *Penicillium glaucum* or *Bacillus lactis aerogenes*.
H. W.

Fermentation Co-enzyme (Co-zymase) of Yeast. IV. K. Myrbäck and H. von Euler (*Z. physiol. Chem.*, 1924, **138**, 1—10).—Further experiments on the purification of the co-enzyme, using mainly the lead acetate method (this vol., i, 918), are recorded. Baryta, in contrast to lead acetate, precipitates

only insignificant amounts of the co-enzyme. Adsorption by alumina gave inconclusive results. Tholin's results (A., 1922, i, 305) on the inactivation of the co-enzyme by heat at varying degrees of acidity have been confirmed with more active preparations.
E. S.

Formation of *l*-Malic Acid in Alcoholic Fermentation by Yeast. H. D. Dakin (*J. Biol. Chem.*, 1924, **61**, 139—145).—*l*-Malic acid is a constant product of the action of yeast on pure sucrose solutions; the amount formed is increased by the addition of sodium hydrogen carbonate to the medium; it is diminished by the addition of monoamino-acids, and of glutamic, aspartic, and hydroxyaspartic acids, also by the products of hydrolysis of yeast; it is little affected by proline and hydroxyproline and is sometimes increased by hydroxyglutamic acid; it is markedly increased by sodium fumarate, but is not affected by sodium succinate. C. R. H.

"Limit" Dextrin and a Complement of the Amylases. III. H. Pringsheim and A. Beiser (*Biochem. Z.*, 1924, **148**, 336—343).—In continuation of previous observations (this vol., i, 106), it is found that amylose is hydrolysed by amylases much more quickly than is amylopectin. The presence of complement does not influence the hydrolysis of amylose, whilst it has a marked accelerating effect on that of amylopectin. "Limit" dextrin ("Grenzdextrin") is a trisaccharide derived from amylopectin (cf. Pringsheim and Wolfsohn, this vol., i, 714). Amylase complement has a marked effect on the hydrolysis of glycogen, a fact supporting the view that amylopectin and glycogen may be related (Pringsheim and Goldstein, A., 1922, i, 633). Complement is associated with malt amylase in the natural state. J. P.

Dextrin-producing Power of Malt Amylase and the Reactivation of Amylase Inactivated by Heat. T. Chrząszcz (*Biochem. Z.*, 1924, **150**, 60—92).—The preparations of amylase were obtained from barley, wheat, and millet, and showed only quantitative differences in their behaviour. The hydrolysis of starch by this amylase proceeds best at p_H 4·66—5·28. The speed of the reaction is increased by using large amounts of enzyme in concentrated solution and by keeping the starch paste as thick as is consistent with thorough mixing with the enzyme. The starch paste is best prepared by heating at a temperature above 80°. The optimum temperature for the reaction is not fixed, but depends on the amount of enzyme present; with small amounts it is 30—50°; with large amounts 50—70°. Amylase is completely inactivated by heating for 2 hours at 90°; such a preparation may be partly reactivated by shaking with air; shaking with oxygen, hydrogen peroxide, or carbon dioxide does not increase the reactivation.
C. R. H.

Isoelectric Point of Malt Amylase. H. C. Sherman, A. W. [illegible], and M. L. Caldwell (*J. Amer. Chem. Soc.*, 1924, **46**, [illegible]).—Working with purified enzyme preparations in [illegible] adjusted to a wide range of hydrogen-ion concentrations by means of buffer solutions, and using the U-tube apparatus of Michaelis (A., 1909, i, 277) suitably modified, the isoelectric point of malt amylase has been determined by electrophoresis to be p_H 4·3—4·5, a point which coincides with its maximum activity towards starch (Sherman, Thomas, and Baldwin, A., 1919, i, 181). On the acid side of this range, the enzyme migrates towards the cathode, on the alkaline side towards the anode. The relative concentration of the enzyme in the anodic and cathodic arms was determined by a modification of Sherman's gravimetric method (A., 1910, ii, 1012; 1922, i, 283). These results show that the enzyme is either an ampholyte or associated with an ampholyte and support the view previously advanced that amylase is either protein in nature or intimately associated with protein. The results are in accord with the observation (Sherman and Thomas, A., 1915, i, 183) that the amylolytic activity of malt amylase is increased by the addition of neutral salts. R. B.

Invertase in Honey. J. M. Nelson and D. J. Cohn (*J. Biol. Chem.*, 1924, **61**, 193—224).—Honeycombs were extracted with water and the filtered solution was treated with alcohol; the viscous precipitate was stirred with a little water and the filtered solution submitted to dialysis; the clear solutions of invertase so obtained were used for a detailed comparison of the mode of action of this invertase with that from yeast. The relative velocities of inversion at different periods of the reaction are not the same with the two enzymes; the optimum p_H for honey invertase is 5·5—6·3 as against 4·4—5·0 for yeast invertase; moreover, for honey invertase the optimum p_H varies with different stages of the reaction, whereas with yeast it is constant throughout. The honey invertase is the less stable towards acid, being partly inactivated at p_H 5·8. The effect of variations in sucrose concentration is similar with both enzymes, the optimum concentration being 4%. C. R. H.

Decomposition of Invertase by Enzymes. I and II. H. von Euler and K. Josephson (*Z. physiol. Chem.*, 1924, **138**, 11—20, 38—48).—Although the physical properties of invertase recall those of proteins (this vol., i, 466, 693, 799; cf., however, Willstätter and Schneider, this vol., i, 692), neither the separate nor successive actions of pepsin and trypsin produced a decrease in the viscosity of a solution of an invertase preparation of high activity (*If*=225) approaching in magnitude that produced in a gelatin solution. Pepsin diminished the activity of the invertase only slightly (14%) in 38 hours; trypsin, however, caused a considerable diminution in 2 days, and after 5 days only 28% of the original activity remained. The authors conclude that invertase is only decomposed with difficulty by proteolytic enzymes, but that when such decomposition does occur the activity of the invertase is simultaneously destroyed; the activity of the invertase complex is thus closely connected with its protein portion. E. S.

Invertase of *Aspergillus flavus*. K. Josephson (*Z. physiol. Chem.*, 1924, **138**, 144—147).—The hydrolysis of sucrose by this mould follows the course of a unimolecular reaction; the curve expressing relationship of rate of hydrolysis to p_H lies between those obtained with the invertases of yeast and of *Penicillium glaucum*. C. R. H.

Lichenin and Lichenase. H. PRINGSHEIM and W. KUSENACK (*Z. physiol. Chem.*, 1924, **137**, 265—271).—The swelling of lichenin is due to the fact that it forms an ester with silicic acid. A lichenin preparation purified by repeated solution and precipitation contained 2·64% of ash which consisted of silica only. The presence of silica as an adventitious impurity in lichenin thus purified is scarcely conceivable. In order to ascertain whether lichenin is entirely composed of cellobiose residues, it was hydrolysed with the lichenase recently found in malt extract (this vol., i, 233), which also contains cellobiase. Further observations now show that cellobiase disappears completely after keeping the malt extract for 6 months, and it then contains lichenase only. When lichenin is hydrolysed with such an extract at 37° and p_H 5, it is quantitatively converted into cellobiose in about 4 days. Cellobiose on acetylation in pyridine solution does not give β-octa-acetylcellobiose, m. p. 228°, but the α-form, m. p. 195°. D. R. N.

Laccase. P. FLEURY (*Bull. Soc. Chim. biol.*, 1924, **6**, 436—448; 449—463).—The oxidation of guaiacol by laccase was studied quantitatively by determining colorimetrically the guaiacoquinone formed. The latter is proportional to the time or the quantity of the enzyme so long as the action is carried out at a moderate temperature and not too far. When the "initial velocity" (or activity) of the enzyme is plotted against the concentration of guaiacol, keeping the quantity of enzyme constant, a curve is obtained which may be divided into two parts, the first in which the velocity is proportional to the quantity of guaiacol, and the second in which it is independent of its concentration. When the amount of laccase is varied, the point of inflexion of the curve is displaced towards lower concentrations with diminishing amounts of laccase. The influence of the oxygen concentration is very similar to that of guaiacol. The results may be explained by assuming a combination between the enzyme and the substrate, or by the influence of the rate of diffusion of oxygen into the medium. D. R. N.

Comparison of Liver Esterase with Pancreatic Lipase. Stereochemical Specificity of Lipases. R. WILLSTÄTTER and F. MEMMEN (*Z. physiol. Chem.*, 1924, **138**, 216—253).—The hydrolytic activity of liver esterase, whether purified or not, towards glycerides is reduced by the addition of such substances as calcium chloride and sodium oleate which favour the action of pancreatic lipase; in the hydrolysis of simple esters the addition of these substances is without effect. A comparison of the rate of hydrolysis of different substances by the enzymes from liver and pancreas of the same animal shows that in the case of olive oil the pancreatic enzyme is enormously more active, whilst in that of methyl butyrate the liver enzyme is the more active. The best purification of the hepatic enzyme was effected by extracting the liver with dilute ammonia, redissolving the crude product, obtained by evaporating this extract, in a solution of acetic acid and ammonium acetate of p_H 4·2, and adsorbing the enzyme on kieselguhr or aluminium hydroxide, from which it was subsequently recovered with dilute ammonia; such preparations are about twenty times as active as the crude desiccated liver; on keeping they lose about one-fifth of their activity in the first few days and thereafter remain almost constant. The activity of the enzyme, especially of the purified preparations, is strongly inhibited by atoxyl, and slightly by quinine.

A series of experiments was made to determine the stereochemical specificity of the two enzymes (cf. Dakin, A., 1904, i, 1071; 1905, i, 556). Pancreatic lipase hydrolysed the lævorotatory component more rapidly in the case of the racemic esters of mandelic, phenylmethoxyacetic, phenylchloroacetic, and phenylbromoacetic acids and the dextrorotatory component of the esters of phenylaminoacetic and tropaic acids and of leucine; with hepatic esterase, on the other hand, the dextrorotatory component was the more rapidly hydrolysed in all the above cases except for the esters of phenylchloroacetic, phenylbromoacetic, and tropaic acids. The degree of specificity of the pancreatic enzyme was the greater throughout. The authors conclude, on the whole, that the two enzymes are distinct from one another. C. R. H.

Enzymic Activity of Lactic Acid Bacteria. II. A. I. Virtanen (*Z. physiol. Chem.*, 1924, **138**, 136—143; cf. this vol., i, 915).—Dried preparations of *Bacillus casei* ε possess the power of synthesising hexosephosphate from solutions containing dextrose and inorganic phosphate, which suggests a similarity between the process of lactic acid fermentation and the formation of lactic acid in muscle. C. R. H.

Activity of Urease in High Concentrations of Alcohol. N. N. Ivanov (*Biochem. Z.*, 1924, **150**, 108—114).—Urea is decomposed, to some extent, by urease in concentrations of alcohol as high as 92·5% and of acetone up to 85%. It is suggested that such solutions, in which the decomposition proceeds much more slowly than in water, may afford suitable media for the study of the intermediate products of the reaction. C. R. H.

Enzymic Hydrolysis of Phenaceturic Acid. C. Neuberg and J. Noguchi (*Biochem. Z.*, 1924, **147**, 370—371).—Takadiastase contains an enzyme capable of hydrolysing sodium phenaceturate with the liberation of phenylacetic acid. J. P.

Phenolases in the Blood. K. Hizume (*Biochem. Z.*, 1924, **147**, 216—220).—There is present in human serum a phenolase capable of oxidising dihydroxybenzene derivatives, which is affected neither by heating at 56° for 30 minutes nor by dialysis. The phenolase is also found in the sera of sheep, rabbits, dogs, and guinea-pigs in amounts diminishing in the order cited. J. P.

Enzymes of the Skin. Y. Yamasaki (*Biochem. Z.*, 1924, **147**, 203—215).—Diastase and lipase are present in human skin in the superficial and deeper layers. The latter enzyme is stable to both quinine and atoxyl and therefore differs from the other lipases of the body. Peptolytic and autolytic enzymes are also present, together with a catalase and an oxidase, the latter being capable of oxidising dihydroxybenzene derivatives but not the monohydroxy compounds. J. P.

Formation of *l*-Leucic Acid in Acetone–Butyl Alcohol Fermentation. E. G. Schmidt, W. H. Peterson, and E. B. Fred (*J. Biol. Chem.*, 1924, **61**, 163—175).—From the solution obtained by the fermentation of maize mash by *Bacillus granulobacter pectinovorum* there were isolated the calcium and zinc salts of an acid, $C_6H_{12}O_3$. On distillation with permanganate this acid gave an aldehyde, which was identified by its *p*-nitrophenylhydrazone and its aldomedon as isovaleraldehyde. The acid was was therefore α-hydroxy*iso*hexoic acid; it gives all the qualitative reactions for lactic acid, and it is suggested that it may have been this acid, and not lactic acid, which was obtained by Speakman (this vol., i, 371) under similar conditions. C. R. H.

Activation of Papain by Hydrocyanic Acid. R. Willstätter and W. Grassmann (*Z. physiol. Chem.*, 1924, **138**, 184—215).—The activating effect of hydrocyanic acid on papain first observed by Mendel and Blood (A., 1910, i, 796) has been studied in a series of experiments on the hydrolysis of gelatin by this enzyme. The rate of hydrolysis is approximately trebled by the addition of cyanide; the optimum temperature for the enzyme is 65—70°, the rate of reaction being nearly doubled by every rise of 10° from 30° to 70°; the optimum reaction, with or without the addition of cyanide, is p_H 5, and it is suggested that the closeness of this optimum reaction to the isoelectric point of gelatin (p_H 4·7) may indicate that this enzyme attacks the undissociated protein molecule. The maximum activation is obtained by allowing the cyanide to act on the enzyme for an hour, before mixing with the gelatin solution; this is true of both crude and purified preparations and of those which, having been once activated with cyanide, have been inactivated again by removal of the hydrocyanic acid; it therefore shows that the activation consists in the formation of a dissociable compound between enzyme and cyanide. The sensitivity of the enzyme to the presence of cyanide is so great that it can be used as a test for the presence of amounts of cyanide of the order of 0·001 mg. Commercial peptone and peptide mixtures prepared by the partial digestion of gelatin are scarcely attacked by papain unless activated by cyanide; pure dipeptides are not hydrolysed even by the activated enzyme. The best purification of the enzyme was effected by adsorption on aluminium hydroxide from an aqueous-alcoholic solution containing ammonia, and subsequent recovery from the precipitate by means of dilute acetic acid. C. R. H.

Asymmetric Enzymic Hydrolysis of Benzoylated Amino-acids. C. Neuberg and K. Linhardt (*Biochem. Z.*, 1924, **147**, 372—376).—Benzoyl-*dl*-glycine and benzoyl-*dl*-alanine are hydrolysed by preparations of takadiastase, the *d*-stereoisomerides being preferentially attacked whilst the *l*-isomerides remain unchanged. Thus it is possible to obtain both antipodes of a racemic amino-acid, since the free *d*-amino-acid may be separated from the benzoyl-*l*-amino-acid and the latter may then be hydrolysed. J. P.

Biochemical Method of Resolving Racemic Amino-acids. C. HOPPERT (*Biochem. Z.*, 1924, **149**, 510—512).—Takadiastase contains an enzyme capable of hydrolysing hippuric acid and its homologues into benzoic acid and the amino-acid. This *amino-acidase* was found by the author to hydrolyse benzoyl-*d*-alanine, but not its stereoisomeride, and he adopted this method for resolving the inactive amino-acid. S. S. Z.

Enzymes of *Utricularia vulgaris*. I. A. N. ADOWA (*Biochem. Z.*, 1924, **150**, 101—107).—Extracts of this insectivorous plant possess a slight power of hydrolysing gelatin and casein. In the case of gelatin, the hydrolysis proceeds best in an alkaline medium; in such a medium the process is inhibited by the addition of calcium chloride and of animal charcoal, but in a neutral medium it is slightly accelerated by these substances. C. R. H.

Occurrence of Catalase in Micro-organisms. A. J. KLUYVER (*Z. physiol. Chem.*, 1924, **138**, 100—101).—It is provisionally concluded that catalase occurs only in those bacteria which use free oxygen in their metabolic processes. E. S.

Destruction of Rennin by Agitation: A Case of Catalysis at an Air–Liquid Interface. E. K. RIDEAL and C. G. L. WOLF (*Proc. Roy. Soc.*, 1924, A, **106**, 97—116).—Agitation of rennin solutions reduces their power of clotting milk. This is traced to the presence of some substance, probably a fatty acid, which reacts chemically with the rennin, mainly at the air–liquid surface where they are both adsorbed and the molecules are orientated favourably for reaction. This substance can be removed by dialysis, and by selective adsorption by fuller's earth or starch, or it can be displaced from the surface by some capillary active substance such as saponin. It can also be rendered innocuous by conversion into a salt. Its effect can be imitated by the capillary-active organic acids or by phenol, but sulphuric acid (not capillary-active) is ineffective. As a result of the reaction the surface tension is increased and the p_H lowered. Dialysed solutions of rennin are less active owing to partial coagulation but may be peptised by small quantities of acid without the p_H being significantly increased. [Cf. *B.*, 1924, 726.] L. J. H.

Mechanism of the Anti-peptic Action of Blood Serum. L. LORBER (*Biochem. Z.*, 1924, **148**, 49—52).—The anti-peptic action of blood-serum is ascribed to the sodium hydrogen carbonate present. J. P.

Efficiency of some Organic Dyes as Anti-ferments. E. H. HARVEY (*Amer. J. Pharm.*, 1924, **96**, 585—589).—The efficiency of a number of organic dyes as anti-ferments has been measured by observing the retardation of the change in rotation produced by their addition to yeast–sucrose solution. The following dyes are arranged in the order of decreasing efficiency: safranine, *p*-nitrophenol, methylene-blue, eosin Y, methyl-violet, cyanine, acid-fuchsin, alizarin-blue S. Mercuric chloride is the most effective anti-ferment, as it kills the yeast cells almost immediately; safranine shows 57·3% efficiency as compared with mercuric chloride, whilst that of alizarin-blue S is practially nil. Ultra-violet light shows an efficiency of 91·8%. R. B.

Action of Uranyl Acetate. II. Action on Various Enzymes. Y. Mikawa (*Biochem. Z.*, 1924, **149**, 540—549).—Uranyl acetate reduces the action of takadiastase, serum diastase, liver diastase, blood catalase, liver catalase, serum lipase, and liver lipase. S. S. Z.

Action of Poisons on Enzymic Processes. IX. Action of Poisons on Metallic Catalysts and Catalase Processes. C. G. Santesson (*Skand. Arch. Physiol.*, 1923, **44**, 262—305; from *Chem. Zentr.*, 1924, i, 1964—1965; cf. A., 1922, i, 1077—1078).—From a consideration of the properties of catalases and metallic catalysts the action of catalases is held to be enzymic and not due to metals present in them. Electrolytes exert a stronger inhibitory effect on colloidal metallic catalysts than on catalases. This may be related to the protective effect of emulsoids, associated with or identical with the catalases. G. W. R.

Action of Simple Narcotics on Succinodehydrogenase. H. Grönvall (*Skand. Arch. Physiol.*, 1923, **44**, 200—214; from *Chem. Zentr.*, 1924, i, 1961).—Methyl alcohol, ethyl alcohol, propyl alcohol, and the butyl alcohols inhibit the activity of succinodehydrogenase (Ohlsson, A., 1922, i, 785). The inhibitory effect increases with the number of carbon atoms. G. W. R.

Action of Urethanes on Succinodehydrogenase. D. Svensson (*Skand. Arch. Physiol.*, 1923, **44**, 306—314; from *Chem. Zentr.*, 1924, i, 1961; cf. preceding abstract).—Methyl-, ethyl-, propyl-, *iso*butyl-, and *iso*amyl-urethanes exert an inhibitory effect, which increases with the molecular weight of the urethane, on succinodehydrogenase. Chloral hydrate is as effective as *iso*butylurethane, whilst phenol and potassium fluoride have a still greater inhibitory power. G. W. R.

Effect of Antipyretics on Succinodehydrogenase and on the Respiration of Tissues. I. I. Nitzescu and J. Cosma (*Compt. rend. Soc. Biol.*, 1923, **89**, 1401—1402, 1406—1407; from *Chem. Zentr.*, 1924, i, 2163).—Sodium salicylate, pyramidone, and antipyrin exert an inhibitory effect on the succinodehydrogenase action of ox muscle on potassium succinate. A similar effect on the respiration of tissues is observed. Urethanes display a similar but weaker effect. G. W. R.

Mechanism of the Action of Amino Promoters on Enzymes. E. W. Rockwood (*J. Amer. Chem. Soc.*, 1924, **46**, [illegible]1615; cf. this vol., i, 351).—The rate of decay of urease and ptyalin in solution, alone, and in the presence of three typical α-amino-acids, glycine, aspartic and hippuric acids, has been measured. The results confirm the view that the promoter effect is only partly due to the prevention of decay of the enzyme, and prove that the promoter acts chiefly through a specific stimulating influence on the enzyme (cf. Sherman and Walker, A., 1923, i, 1033). R. B.

Autolysis. XI. Relation of the Isoelectric Point to Digestibility. A. B. HERTZMAN and H. C. BRADLEY (*J. Biol. Chem.*, 1924, **61**, 275—287).—Addition of proteins to autolysing liver increases the amino-acid production at and above a certain hydrogen-ion concentration which is specific to each protein and almost coincident with its isoelectric point. This is taken to be evidence that in order to be digested by liver proteases, proteins must be in the form of acid salts, and it explains the previous observation (A., 1916, i, 582) that addition of acid stimulates autolysis. C. R. H.

Autolysis. II. Effect of Iodine on the Autolysis of Organs. O. STEPPUHN and L. UTKIN-LJUBOVZOV (*Biochem. Z.*, 1924, **150**, 165—172; cf. A., 1923, i, 1158).—Autolysis of serum, liver, lungs, and kidneys is accelerated by small amounts of iodine and delayed by large amounts; tryptic digestion of casein is delayed by iodine in all concentrations. C. R. H.

Oligodynamic Properties of Insoluble Mercury Compounds. S. REBELLO (*Compt. rend. Soc. Biol.*, 1923, **88**, 1333—1335; from *Chem. Zentr.*, 1924, i, 924—925).—Mercury and insoluble mercury compounds (with the exception of mercuric sulphide) exert an inhibitory effect on bacterial growth by diffusion in gel cultures. G. W. R.

Properties of Diphtheria Anatoxin. G. RAMON (*Compt. rend.*, 1924, **179**, 422—425).—Diphtheria anatoxin differs from the original toxin in having lost toxicity (cf. this vol., i, 463) and possessing a greater resistance to heat. Preparations of the anatoxin retained their strength, as measured by the amount of antitoxin required to cause flocculation, without sensible variation when kept at 3° to 4° for a year. The rate of flocculation is slightly diminished, and this effect is a little more pronounced when the anatoxin is kept at laboratory temperature (20°). The length of time for which the preparations were kept was without appreciable effect on their immunising or hyperimmunising power, *in vivo*, and in no case was any return of toxicity observed, even after the lapse of a year. Anatoxin preparations warmed at 65° or 70° for 1 hour retained their full flocculating and immunising powers, the appearance of the flocculation being more or less retarded, and these properties begin to decrease only when the preparation is heated at 72—75°. R. B.

Effect of Oxidising Agents on Diphtheria Toxin. F. DE POTTER (*Compt. rend. Soc. Biol.*, 1923, **89**, 422—425; from *Chem. Zentr.*, 1924, i, 930).—Diphtheria toxin is oxidised only with difficulty even by ozone and potassium permanganate. G. W. R.

Yeast Protein as Antigen. H. Lüers and F. Ottensooser (*Biochem. Z.*, 1924, **148**, 130—146).—From dried yeast, the proteins cerevisin and zymocasein were isolated in yields of 10% and 3%, respectively. They can be differentiated by crossed precipitin reactions, from which it is concluded that their specificity as antigens has primarily a chemical basis. Anaphylaxis experiments reveal the presence of yeast proteins as well as those of barley in the precipitate formed during the pasteurisation of beer. J. P.

Products of the Catalytic Degradation of the Feathers of the Goose. Remarks on W. S. Ssadikov and N. D. Zelinsky's Work. E. Abderhalden (*Biochem. Z.*, 1924, **149**, 572—574).—Polemical. S. S. Z.

Preparation of Insulin. H. Pénau (*J. Pharm. Chim.*, 1924, **30**, 145—153).—Impure insulin is obtained from the pancreas by extraction with alcoholic hydrogen chloride, removing fatty impurities and a portion of the salts and proteins, and precipitation with absolute alcohol. It is purified by saturating its solution with sodium chloride, centrifuging, and dialysing the solution of the solid so obtained. The insulin so obtained does not cause harmful secondary reactions. [Cf. *B.*, Oct. 31.] W. T. K. B.

Preparation of Insulin and its Physiological Action. C. Serono, E. Trocello, and A. Cruto (*Rassegna Clin. Terap. Sci. aff.*, 1923, **22**, 243—247; from *Chem. Zentr.*, 1924, i, 1409).—Directions are given for the preparation of insulin free from diastase. It is stated that methæmoglobin occurs in the blood of rabbits under the influence of insulin. G. W. R.

Preparation of Insulin. A. Sordelli and V. Deulofeu (*Compt. rend. Soc. Biol.*, 1923, **89**, 743—744; from *Chem. Zentr.*, 1924, i, 1234).—The precipitate in 0·1—0·2*N* picric acid is purified by washing with acetone. The picric acid may also be removed by adsorption on silk. G. W. R.

Metabolin and the Internal Secretion of the Pancreas. E. Vahlen (*Münch. med. Woch.*, 1924, **71**, 101—102; from *Chem. Zentr.*, 1924, i, 2178).—"Irreversible" metabolin (Gehe's "irrebolin") is effective against adrenaline glycosuria in rabbits when administered per os, and still more effective per rectum. Insulin is held to inhibit the formation of sugar in the liver, whilst "irrebolin" increases the oxidation of sugar. The complete function of the inner secretion of the pancreas is due to a combination of the actions of these two hormones. G. W. R.

Yeast Growth Promoting Vitamin Tested on Animals. J. Deas (*J. Biol. Chem.*, 1924, **61**, 5—8).—An infusion of malt combings, which has been shown to contain the "bios" described by Wildiers (*La Cellule*, 1901, **18**, 313) and which is apparently identical with the vitamin-*D* of Funk and Dubin (A., 1922, i, 203), [illegible] administered to rats in combination with a diet free from [illegible] *B*, does not promote their growth. The "bios" and [illegible] *B* are therefore not identical. C. R. H.

Comparative Physiological Importance of Iron and Zinc. G. Bertrand and H. Nakamura (*Compt. rend.*, 1924, **179**, 129—133; cf. A., 1922, i, 893).—It has already been shown that when a litter of young mice was divided into two groups, one of which was fed on a diet free from vitamins and also completely free from zinc, the other on a diet free from these vitamins but containing small quantities of zinc, the life of the latter group was prolonged 25—50% beyond that of the former. The experiments have now been repeated with both groups receiving zinc but only one group receiving iron. In only one experiment in a series of six did the iron-fed mice survive the others, and the presence of iron in the diet has not therefore the marked effect of that of zinc. F. G. M.

Colloidal Properties of Phloridzin. R. Schaefer and F. Schmidt (*Biochem. Z.*, 1924, **149**, 585—591).—Phloridzin diffuses very slowly through gelatin gels. Solutions of widely differing concentrations do not produce any perceptible lowering of the freezing point and display a strikingly low conductivity. The addition of alkali or acid does not alter its degree of dissociation. A Tyndall cone is observed in phloridzin solutions of considerable dilutions and colloidal particles can be seen with the immersion ultramicroscope. By means of the ultra-filter the dimensions of these particles are found to be probably smaller than 10 $\mu\mu$.

S. S. Z.

Characters and Composition of Mustard Oil. J. C. Delage (*Ann. Falsif.*, 1924, **17**, 336—343).—Specimens of mustard oil examined had *d* 1·0186 to 1·0237 and contained from 96 to 97·7% of allylthiocarbimide. On fractional distillation from a few drops to 7% distils at 148·5° to 149·9°; the greater part distils at 150—150·5° (pure allylthiocarbimide) and the residue amounts to 1 to 2%. The composition of mustard oil varies with its age; the maximum amount of allylthiocarbimide is present a few months after its preparation, and then decreases. W. P. S.

Insecticidal Principle in *Chrysanthemum cinerariæfolium*. IV. Insecticidal Principle Produced on Dry Distillation of *Chrysanthemum cinerariæfolium*. R. Yamamoto and M. Sumi (*J. Chem. Soc. Japan*, 1923, **44**, 1070—1085).—By distilling powdered flowers of *Chrysanthemum cinerariæfolium* at 260—280°, an acidic distillate was obtained, in which the following compounds were found: Acetic and propionic aldehydes and acids, methyl-, trimethyl-, butyl-, and amyl-amines, pyridine and a homologue of pyridine (picrate, m. p. 84°; chloromercurate, m. p. 125°). For determining the insecticidal power of these compounds, the effects of homologous acids, esters, and bases were compared on flies and other insects. When naturally evaporated, formic acid is more potent than any other fatty acid; butylamine and *tert.*-amylamine have the strongest action amongst amines. In the case of aliphatic amines boiling below 80°, the insecticidal power is proportional to the molecular weight. When evaporated by heating or eaten by insects, nicotine is the most toxic of the substances investigated. Generally cyclic compounds have greater power than aliphatic substances. K. K.

Chemistry of Grape Pigments. II. Anthocyans in Clinton Grapes. R. J. ANDERSON and F. P. NABENHAUER (*J. Biol. Chem.*, 1924, **61**, 97—107; cf. this vol., i, 251).—The anthocyanin of Clinton grapes has been isolated and appears to be identical with that obtained by Willstätter and Zollinger from *Vitis riparia* (A., 1917, i, 47). It was isolated as the *picrate* which was converted into an amorphous *chloride*, $C_{23}H_{35}O_{12}Cl,2H_2O$. On boiling with hydrochloric acid it gives dextrose and crystalline *anthocyanidin chloride*, $C_{17}H_{15}O_7Cl,1{\cdot}5H_2O$. On boiling with hydriodic acid this yields delphinidin iodide; the methoxyl content is intermediate between those required by a mono- and a di-methyl ether of delphinidin. Phloroglucinol was isolated from the products of alkali fusion of the anthocyanidin chloride; the latter, on boiling with acetic anhydride, gave an acetyl derivative (m. p. 205—210°); this, on oxidation with permanganate, gave an ether-soluble substance from which, by hydrolysis with hydriodic acid, gallic acid was obtained. C. R. H.

Presence of Valine in Zein. H. D. DAKIN (*J. Biol. Chem.*, 1924, **61**, 137—138).—The presence of valine in zein, recorded by Osborne and co-workers (A., 1908, i, 115; 1910, i, 598), is confirmed by the isolation of about 1% of pure crystalline valine after hydrolysis of zein by boiling with dilute sulphuric acid. The author suggests that his own previous failure to detect valine in this protein (A., 1923, i, 1243) may have been due to racemisation owing to the high temperature at which the hydrolysis was carried out. C. R. H.

Optically Active Asparagine in Seedling Lupins. A. PIUTTI (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 384—386; from *Chem. Zentr.*, 1924, i, 1941).—*d*-Asparagine was obtained together with small quantities of *s*-asparagine from lupin seedlings. G. W. R.

Henna. O. A. OESTERLE (*Schweiz. Apoth.-Ztg.*, 1923, **61**, 541—543; from *Chem. Zentr.*, 1924, i, 1388).—From a hot alcoholic extract of henna, mannitol and tribenzacetal were isolated. It is possible that mannitol is not a normal constituent of henna. G. W. R.

Ternary Materials of Green and Etiolated Leaves. H. COLIN and H. GRANDSIRE (*Compt. rend.*, 1924, **179**, 288—291).—The green leaves of the variegated chestnut always contain starch, which is absent from the etiolated leaves, and a larger proportion of both sucrose and reducing sugars than the latter. The sugars of etiolated leaves contain a larger proportion of dextrose. At midsummer a dextrorotatory, non-reducing sugar, which is oxidised by nitric acid to mucic acid and which, after the action of invertase, is slowly hydrolysed by emulsin, appears in the green leaves and increases in quantity up to 0·5% as the season advances. No such product is found in etiolated leaves. Both green and etiolated leaves contain at least two glucosides, æsculin and fraxin, and the quantity of fatty materials is practically the same in both. The green leaves, however, contain a larger quantity of pectins which are precipitated by alcohol, baryta, and basic lead acetate and on hydrolysis yield arabinose. J. W. B.

Essence of Iris. P. LANGLAIS and J. GOBY (*Compt. rend.*, 1924, **179**, 173—175).—The acidic constituents of iris essence have been separated by fractional distillation into octoic acid, b. p. 110—111°/4 mm., *anilide*, m. p. 51°; nonoic acid, b. p. 124—125°/4 mm., *anilide*, m. p. 57°; decoic acid, b. p. 138—139°/4 mm., *anilide*, m. p. 65·5°, ethyl ester, b. p. 104°/4 mm., d^{28} 0·859; undecoic acid, b. p. 145—146°/4 mm., *anilide*, m. p. 71°; dodecoic acid, b. p. 153—154°/4 mm., *anilide*, m. p. 75·5°; tridecoic acid, *anilide*, m. p. 81·5°. This is claimed to be the first occasion on which nonoic, undecoic, and tridecoic acids have been found in natural products. F. G. M.

Phytosterols of Wheat Endosperm. R. J. ANDERSON and F. P. NABENHAUER (*J. Amer. Chem. Soc.*, 1924, **46**, 1717—1721; cf. this vol., i, 924).—The unsaponifiable matter from the fat extracted from wheat endosperm has been separated into an unsaturated sterol, identical with sitosterol, a saturated sterol, dihydrositosterol, $C_{27}H_{47}OH$, m. p. 144—145°, $[\alpha]_D^{20}$ +25·82° (in chloroform), and a non-crystallisable oil which has not been examined. The two sterols cannot be separated by crystallisation of their bromination products from alcohol, but are readily separated by treatment with acetic anhydride and sulphuric acid. The dihydrositosterol gives an acetyl derivative, m. p. 140°, and appears to be identical with the saturated sterol occurring in maize endosperm. The sterol is present throughout the wheat endosperm, but especially in the bran. R. B.

Effect of Germination on the Aleurone Layer. E. B. BENNION (*Cereal Chem.*, 1924, **1**, 179—183).—A section of the aleurone layer from an ungerminated wheat grain placed on purified starch and kept moist showed no diastatic action in 8 days. From this and other experiments, it is concluded that the aleurone cells of the wheat grain are not glandular in the same sense as the epithelial cells of the scutellum; they provide a reserve food supply but do not function until 6 days after germination.

Analyses of barley and wheat after definite periods of germination showed a gradual decrease in nitrogen content after 30 hrs. Subsequently, in the case of wheat, after about 220 hrs. there is a rapid increase in percentage of nitrogen due to the complete utilisation of the starch in the endosperm. During the early stages of germination, amides formed by the degradation of proteins are further broken down and ammonia is evolved. C. I. G.

Zinc and Copper Compounds of Phæophytin. R. WILLSTÄTTER and K. SJÖBERG (*Z. physiol. Chem.*, 1924, **138**, 171—176).—By the action of zinc acetate in glacial acetic acid solution a compound was obtained containing 1 mol. of zinc to 2 mols. of phæophytin; in pyridine solution 1 mol. of zinc combined with 1 mol. of phæophytin. Two copper compounds were prepared in similar ways, both of which contained 1 mol. of copper to 1 mol. of phæophytin. On hydrolysis with methyl-alcoholic potassium hydroxide, both zinc compounds gave zinc compounds of phytochlorin E and phytorhodin G which were easily decomposed by hydrochloric acid; the copper compound prepared in glacial acetic acid behaved similarly, but that prepared in pyridine solution gave copper derivatives of the hydrolysis products which were very stable towards hydrochloric acid. C. R. H.

Wine Yeasts. E. KAYSER and H. DELAVAL (*Compt. rend.*, 1924, **179**, 295—297).—The authors have isolated and described several strains of red yeasts from the vine " Breton," two of which are bottom yeasts, producing red colonies, and a third a top yeast forming pigments most intensely in the presence of slightly fermentable or non-fermentable sugars. These yeasts liquefy gelatin, and ferment lævulose, dextrose, and sucrose, but neither lactose nor raffinose. They ferment lævulose more readily than dextrose, the reverse being the case with a colourless yeast of the same origin. They are equally sensitive to the presence of nitrogenous substances (cf. Kayser, A., 1912, ii, 861) and produce a relatively larger proportion of volatile esters than does the colourless yeast. The ratio of valeric acid to acetic acid in the case of the red yeasts is also twice that obtained with the colourless variety. J. W. B.

Formation of Starch from Sugar by the Leaves of Higher Plants. A. W. REINHARD (*Compt. rend. Soc. Biol.*, 1923, **89**, 1274—1275; from *Chem. Zentr.*, 1924, i, 1548).—The leaves of beans, peas, and white acacia produce starch when immersed in 10% sugar solution and exposed to light. G. W. R.

Transformation of Hydrocyanic Acid by Plant Sap. S. DEZANI (*Biochim. terap. sperim.*, 1923, **10**, 85—96; from *Chem. Zentr.*, 1924, i, 2159).—Plant sap produces substances which on treatment with alkalis yield ammonia from hydrocyanic acid. This property is not shown by fermented plant juices or after addition of dextrose on account of the high acidity produced. G. W. R.

Reactions of the Alga *Chondrus crispus*, particularly with certain Dyes used in Therapy. E. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1924, **30**, 154—161).—The action of various acids, bases, salts, and dyestuffs on an aqueous extract of the alga is described. Flocculation is caused by azines (*e.g.*, safranine) and thiazines (*e.g.*, methylene-blue), but not by oxazines (*e.g.* Meldola's blue) nor by methyl violet or magenta. W. T. K. B.

Detection of Acids in Plants. II. H. SCHMALFUSS and K. KEITEL (*Z. physiol. Chem.*, 1924, **138**, 156—163).—A detailed description is given of a method of qualitative separation of the acids which may be obtained from plants, and also of micro tests for certain individual acids. C. R. H.

Method for Preparing Large Quantities of Yeast Nucleic Acid as a Magnesium Compound. E. J. BAUMANN (*J. Biol. Chem.*, 1924, **61**, 1—4).—Yeast is extracted with water, the solution made alkaline with sodium hydroxide, then partly neutralised with hydrochloric acid, and finally acidified with acetic acid; to the filtered solution is added magnesium sulphate to make 5% concentration and hydrochloric acid until precipitation is complete. The preparations so obtained are protein-free, but contain somewhat less than the theoretical nitrogen and phosphorus; the yield is 0·6 to 1·2% of the fresh yeast. C. R. H.

Feeding of Plants with Aldehydes. V. Influence of Formaldehyde on the Function of Plant Enzymes. T. SABALITSCHKA (*Biochem. Z.*, 1924, **148**, 370—382).—Germination of seeds is inhibited more or less completely by 0·13% formaldehyde solution, whilst the growth of young twigs is somewhat affected by 4% solutions, and the fermentation of dextrose by living yeast is stopped by 0·3% formaldehyde and slowed by concentrations between 0·3 and 0·005%. In the cell sap of plants grown in atmospheres containing formaldehyde less than 0·055% of the aldehyde was found. In general, no evidence was forthcoming in support of the view that in such concentrations the aldehyde acts as a stimulant of plant metabolism. J. P.

Composition and Digestibility of Lupins and Lupin Offals, before and after the Removal of the Bitter Principle; and the Loss of Crude and Digestible Foodstuff resulting from Different Processes of Removal of the Bitter Substances. F. HONCAMP, E. MÜLLER, F. POMMER, and R. SOIKA (*Landw. Versuchs-Stat.*, 1924, **102**, 261—307).—Lupins, after removal of the bitter contents, have a high food value and the milling offals (excepting the "bran") are characterised by a high content of digestible protein. Losses in food value occasioned by the elimination of the bitter flavour, fall mostly on the nitrogen-free extractives, mineral matter, and to a less extent on easily soluble amides. The proteins are but little affected. A. G. P.

Lime Requirement of Soils, and a New Method of Mechanical Analysis. A. N. SOKOLOWSKI (*Arb. Wiss. Inst. Düngemittel*, 1923, **13**, 1—22; from *Chem. Zentr.*, 1924, i, 1584).—Adsorbed calcium is removed from soils by leaching with alkali salts. The soil thereby becomes deflocculated and water extracts from it an "active sediment" which is considered to be its most important constituent. Directions are given for the determination of this material in soils. From the content of a soil in adsorbed calcium and its saturation capacity for calcium and ammonium respectively, a formula for the lime requirement is developed. G. W. R.

Effect of Manganese on Vegetation. G. D'IPPOLITO (*Staz. Sperim. agrar. ital.*, 1923, **56**, 386—400; from *Chem. Zentr.*, 1924, i, 952).—Marked increases in yield were obtained in pot and field experiments when manganese compounds were used as fertilisers. Manganese dioxide was more effective than manganic sulphate. G. W. R.

Determination of the Availability of Fertilisers. C. LUMIA (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 370—371; from *Chem. Zentr.*, 1924, i, 2003).—A method is proposed for determining the availability of fertilisers by comparing their effect with that of water-soluble fertilisers on the activity of brewer's yeast. G. W. R.

Dependence of Denitrification on the Reaction of the Medium. T. M. SSACHAROWA (*Arb. Wiss. Inst. Düngemittel.*, 1923, **15**, 1—22; from *Chem. Zentr.*, 1924, i, 2000).—In culture media the optimum reaction for denitrification lies between p_H 7·0 and p_H 8·2. This process does not occur below p_H 5·5 or above p_H 9·8. The optimum for the decomposition of nitrites lies between p_H 5·5 and p_H 7·0. G. W. R.

Chemical and Biological Studies with [Calcium] Cyanamide and some of its Transformation Products. K. D. JACOB, F. E. ALLISON, and J. M. BRAHAM (*J. Agric. Res.*, 1924, **28**, 37—69).—Under laboratory conditions, ammonification of calcium cyanamide in soil is rapid, but nitrification follows only slowly, probably owing to the formation of small quantities of dicyanodiamide which, when added to soil, inhibits the process of nitrification. Guanyl carbamide and guanidine salts also tend to inhibit nitrification. [Cf. *B.*, 1924, 842.] C. T. G.

Critical Note on Method of Correcting Protein Digestion Coefficients. H. E. WOODMAN (*J. Agric. Sci.*, 1924, **14**, 428—434).—The method of Pfeiffer for correcting "apparent" protein digestion coefficients for the undigested protein in the fæces is adversely criticised. Figures are recorded illustrating anomalous results which may be obtained by the adoption of this correction. A. G. P.

Organic Chemistry.

Superheating of Uniform Organic Compounds. I. Arylparaffins and Aliphatic Esters. S. Skraup and F. Nieten.—(See i, 1185.)

Condensation of Acetylene with Hydrogen Sulphide in Presence of Aluminium Oxide. A. E. Tschitschibabin and O. S. Bagdassarjanz (*J. pr. Chem.*, 1924, [ii], **108**, 200—208).—When acetylene (2 vols.) and hydrogen sulphide (1 vol.) are passed over aluminium oxide at 425—450°, a liquid product is obtained, consisting of thiophen (40%), 2- and 3-ethylthiophen, mercaptans, unsaturated hydrocarbons, and products of b. p. above 186°. The catalyst loses its activity rapidly; the specific gravity of the crude condensation product decreases as the catalyst ages. (Cf. Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 709.)

F. G. W.

Action of Alkali on Ethyl Alcohol and the "Nitric Oxide Reaction" of W. Traube. M. Stechow (*Ber.*, 1924, **57**, [*B*], 1611—1615).—Contrary to previous assumptions, the action of nitric oxide on an alcoholic solution of sodium ethoxide or hydroxide leads invariably to the production of considerable amounts of the compound, $CH_2[N(NO)\cdot ONa]_2$, identical with the product isolated by Traube by the action of nitric oxide on a solution of acetone in alcohol in the presence of alkali. The production of the salt depends entirely on the quantity of alkali present and the duration of the experiment; it ceases with exhaustion of the alkali, but starts again after addition of further amounts of the latter. The source of the product is unknown, but it is significant that the protracted action of alkali ethoxide or hydroxide on ethyl alcohol in the absence of oxygen leads to the formation of resin acids, acetaldehyde, acetic acid, and condensation products of acetone such as mesityl oxide, phorone, and mesitylene. Traube's reaction is therefore unsuitable for the elucidation of constitutional problems.

H. W.

Vapour-pressure Curves for Systems containing Alcohol, Ether, and Water. E. A. Louder, T. R. Briggs, and A. W. Browne (*Ind. Eng. Chem.*, 1924, **16**, 932—935).—By the static method (the apparatus is described and figured), the vapour pressures of ethyl alcohol and of ethyl ether have been determined for the temperature range 0—50°. The values obtained are generally a little higher (about 0·5 mm. for ether, 0·5—1 mm. for alcohol) than those of Ramsay and Young or of Regnault. The vapour pressures of mixtures of (i) alcohol and ether, (ii) alcohol, ether, and water, and (iii) alcohol (95%), ether, and diphenylamine, were also measured over the same temperature range.

W. A. S.

Pyrogenic Decomposition of Propyl Alcohol. (MLLE.) E. PEYTRAL (*Bull. Soc. chim.*, 1924, [iv], **35**, 960—964; cf. A., 1920, i, 217).—By the methods previously employed (A., 1918, i, 1), it is shown that propyl alcohol when passed through a platinum tube at high temperatures undergoes the two primary decompositions: $CH_2Et{\cdot}OH{=}Et{\cdot}CHO{+}H_2$ and $CH_2Et{\cdot}OH{=}CHMe{:}CH_2{+}H_2O$, the former reaction, which requires the least deformation of the molecule, slightly preponderating. The propaldehyde undergoes further decomposition to give ethane and carbon monoxide, whilst the ethane is partly decomposed to ethylene and hydrogen. A small quantity of acetylene is also formed, probably by decomposition of ethylene, and traces of formaldehyde were detected, probably due to the primary decomposition: $CH_2Et{\cdot}OH{=}H{\cdot}CHO{+}C_2H_6$. R. B.

Components of Wood Spirit Oil. II. H. PRINGSHEIM and A. GORGAS (*Ber.*, 1924, **57**, [*B*], 1561—1566; cf. A., 1923, i, 1052).—The portion of the oil, b. p. 90—130°, which is not attacked by sodium hydrogen sulphite has been separated into four components: (1) Δ^{α}-buten-γ-ol, b. p. 97°, characterised by oxidation to pyruvic acid and by reduction to *sec.*-butyl alcohol; (2) diethyl ketone; (3) 2 : 5-dimethyltetrahydrofuran, b. p. 108°, characterised as the ferrocyanide, and (4) 2-methyl-5-ethyl-4 : 5-dihydrofuran, m. p. 125°, which is converted by warm water into ethyl γ-hydroxy-*n*-butyl ketone. A method is given for the determination of methyl propyl ketone and diethyl ketone in mixtures which depends on the difference between their velocities of oximation. H. W.

Dilution of Ethylene Bromohydrin with Water. J. READ and G. J. BURROWS (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 54—57; cf. T., 1920, **117**, 1214).—When water is added to ethylene bromohydrin, a negative thermal effect is produced up to a dilution of about 80% followed, at about 75%, by a positive thermal effect which persists to a dilution of about 10%. Conversely, on adding small amounts of ethylene bromohydrin to water the initial positive thermal effect is followed by a negative effect. The density–concentration curve is regular and of the same type as the refractive index–concentration curve (cf. *loc. cit.*). At 20°, a maximum contraction (1·07%) occurs at a concentration of about 50%, and at 25°, at a concentration of about 46% of ethylenebromohydrin. The viscosity of solutions increases regularly with an increasing proportion of the bromohydrin. W. T. K. B.

Pyrogenic Decomposition of Ethyl Ether. (MLLE.) E. PEYTRAL (*Bull. Soc. chim.*, 1924, [iv], **35**, 964—968).—When the vapour of ethyl ether is passed rapidly through a platinum tube at high temperatures, the only primary reaction is its decomposition into ethane and acetaldehyde. The latter substance undergoes secondary decomposition into carbon monoxide and methane as previously shown (A., 1920, i, 217), whilst the ethane partly decomposes into ethylene and hydrogen, a fraction of the ethylene undergoing a tertiary decomposition to acetylene and hydrogen when the velocity of the gas through the tube is relatively low. Decomposition of the ether to give water and 2 mols. of ethylene or 1 mol. of *cyclo*butane either does not take place or occurs only to a negligible extent, the primary decomposition being thus that which involves the least deformation of the molecule. R. B.

Decomposition of Ethers by Metallic Sodium. II. Relative Tenacity of Different Radicals to the Oxygen Atom. P. SCHORIGIN.—(See i, 1185.)

Glyceryl Tri-*m*-nitrobenzoate. F. STATHER (*Ber.*, 1924, 57, [*B*], 1392—1393).—*Glyceryl tri*-m-*nitrobenzoate*, m. p. 130° (corr.), is prepared by the action of *m*-nitrobenzoyl chloride on glycerol in the presence of chloroform and quinoline. The substance, m. p. 161°, described under this name by Bauer (this vol., i, 825) is probably *m*-nitrobenzoic anhydride. The interchange of acyl radicals during the acylation of mono- or di-glycerides in the presence of quinoline has not yet been observed. H. W.

Behaviour of Esters of Metaphosphoric Acid and of Phosphorous Acid towards Hydrazine, Hydroxylamine, and their Derivatives. W. STRECKER and H. HEUSER (*Ber.*, 1924, 57, [*B*], 1364—1372).—The action of an excess of hydrazine hydrate causes hydrolysis of metaphosphoric esters. If, however, molar quantities of the reactants are brought together in chloroform solution, *ethyl hydrogen orthophosphorhydrazide*,

$$O:P(OH)(OEt)\cdot NH\cdot NH_2,$$

a viscous, multimolecular liquid, is produced. *Ethyl hydrogen orthophosphorphenylhydrazide*, m. p. 192°, and *ethyl hydrogen orthophosphor*-p-*tolylhydrazide*, m. p. 195°, are similarly produced. *p*-Bromophenylhydrazine forms the corresponding p-*bromophenylhydrazide*, m. p. 187°, with considerably greater difficulty, whereas *p*-nitrophenylhydrazine does not appear to react. Highly purified hydroxylamine and ethyl metaphosphate yield *ethyl hydrogen phosphorhydroxylamide*, $O:P(OH)(OEt)\cdot NH\cdot OH$, a syrupy liquid, but derivatives such as phenylhydroxylamine do not react.

Ammonia does not react with triphenyl or tri-*p*-tolyl phosphite at the atmospheric temperature, whereas hydrolysis takes place under more energetic conditions. Similarly, hydrazine hydrate is inactive in the cold, but when warmed yields a mixture of hydrazine phenoxide or *p*-tolyloxide and *dihydrazine hydrogen phosphite*, $P(OH)_3,2N_2H_4,H_2O$, m. p. 105°. The use of halogenated phosphorous esters facilitates but does not alter the character of this reaction. Thus the monohalogenated ester, $PCl(OEt)_2$, gives ammonium chloride, ammonium phosphite, and phenol with ammonia, whilst with hydrazine hydrate it yields dihydrazine hydrogen phosphite, hydrazine phenoxide, and hydrazine hydrochloride. The dichloride, $PCl_2(OEt)$, gives the same products with greater readiness. Triethyl phosphite is not affected by hydrazine hydrate, possibly on account of its relatively low boiling point, whereas diethyl hydrogen phosphite gives dihydrazine hydrogen phosphite. The presence of a halogen atom attached to phosphorus facilitates the hydrolysis.

The normal esters of orthophosphoric or thiophosphoric acid do not react with hydrazine or ammonia. If, however, a halogen atom is present in place of an organic residue, it suffers replacement with production of the corresponding amide or hydrazide. The following new compounds are thus produced: p-*Tolylthiophosphordiamide*, $S{:}P(NH_2)_2{\cdot}O{\cdot}C_6H_4{\cdot}Me$, m. p. 84°; *phenylthiophosphordihydrazide*, $S{:}P(NH{\cdot}NH_2)_2{\cdot}O{\cdot}Ph$, m. p. 95°; p-*tolylthiophosphordihydrazide*, m. p. 106°; *phenylorthophosphordihydrazide*. H. W.

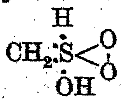
Sulphoxyl Compounds. XIII. Reduction of Aldehydesulphoxylates. A. Binz, C. Räth, and E. Walter (*Ber.*, 1924, **57**, [*B*], 1398—1403; cf. A., 1921, i, 30).—The oxidising action of aldehydesulphoxylates is illustrated by the production of the corresponding disulphides from formaldehydesulphoxylate and thiophenol or *o*-thiocresol, and from formaldehydesulphoxylate which has been condensed with *o*-anisidine or methylamine and thiophenol and ethyl mercaptan. Sodium formaldehydesulphoxylate is reduced by hypophosphorous acid or, in a more complex manner, by hydrogen sulphide to *bishydroxymethyl disulphide*, $OH{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2{\cdot}OH$, m. p. 155°, the yields being poor. Better results are obtained when the sulphoxylate is previously condensed with a secondary amine; thus, formaldehydesulphoxylate, piperidine, and hypophosphorous acid or hydrogen sulphide give *dipiperidinomethyl disulphide*, $S_2(CH_2{\cdot}NC_5H_{10})_2$, m. p. 42° (*hydrochloride*, m. p. 176°). *Diphenylhydroxymethyl disulphide*, $S_2(CHPh{\cdot}OH)_2$, m. p. 65° (decomp.), from benzaldehyde sulphoxylate and hypophosphorous acid, is decomposed by cold sodium hydroxide into sodium disulphide and benzaldehyde and by boiling hydrochloric acid into benzaldehyde, hydrogen sulphide, and sulphur. *Dibenzylmethylaminomethyl disulphide*,

$$S_2(CH_2{\cdot}NMe{\cdot}CH_2Ph)_2,$$

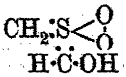
a yellow liquid (*hydrochloride*, m. p. 135°), and *di-2-methylpiperidinomethyl disulphide*, a viscous liquid which gives a crystalline *hydrochloride*, are described.

The constitution, $HO{\cdot}CH_2{\cdot}O{\cdot}S{\cdot}OH$, does not adequately explain the reduction of formaldehydesulphoxylate or the apparently dibasic nature of the substance (cf. Forke, *Diss.*, Berlin, 1923). Formaldehydesulphoxylic acid and diformaldehydesulphoxylic acid (Binz, A., 1918, i, 4) more probably have the constitutions I and II, respectively.

(I.)



$$\mathrm{CH_2{:}\overset{H}{\underset{OH}{S}}{<}\begin{matrix}O\\|\\O\end{matrix}}$$



$$\mathrm{\underset{H\cdot C\cdot OH}{CH_2{:}S}{<}\begin{matrix}O\\|\\O\end{matrix}}$$

(II.)

H. W.

Complex Compounds of Lead Acetate [and Propionate] and the Corresponding Salts of the Metals of the Alkaline Earths. R. Weinland and E. Bauer (*Ber.*, 1924, **57**, [*B*], 1508—1514).—In a previous communication (Weinland and Stroh, A., 1922, i, 981), it has been shown that lead forms with acetic acid residues polynuclear acetato cations. Salts are now described in which the lead atoms are partly replaced by other metallic atoms.

Lead sodium acetate nitrate, $[PbAc_2Na]NO_3,H_2O$, is prepared by the spontaneous evaporation of an aqueous solution of lead acetate and sodium nitrate. The following *salts* are prepared in a similar manner: (1) $[Pb_2(CH_3{\cdot}CH_2{\cdot}CO{\cdot}O)_4Na]ClO_4$;
(2) $[Pb(OAc)_2Sr](ClO_4)(OAc),4H_2O$;
(3) $[Pb_2(CH_3{\cdot}CH_2{\cdot}CO_2)_2(OH)_2Na](ClO_4)(C_3H_5O_2)$,
(4) $Pb(C_3H_5O_2)_2,Pb(OH)_2,NaC_3H_5O_2,NaClO_4$;
(5) $[Na_2(OAc)_2Ba](NO_3)_2,2H_2O$; (6) $[Ba(OAc)_2Mg](ClO_4)_2$. These are all colourless, well-crystallised compounds of which (2) and (6) can be recrystallised unchanged from water.

Calcium and strontium resemble lead in their ability to yield acetato cations, which is established by the isolation of the *salts*: $[Ca(OAc)_2Ca](ClO_4)_2,2H_2O$; $[Sr(OAc)_2Sr](ClO_4)(OAc),4H_2O$; $[Sr(OAc)Sr](NO_3)_2,3H_2O$.

Lead propionate has hitherto been described as non-crystalline. The isolation of a crystalline *salt* containing half a molecule of water of crystallisation causes it to be regarded as the propionate of a lead-propionato base, $[Pb(C_3H_5O_2)_2Pb]C_3H_5O_2,H_2O$. This hypothesis is supported by the isolation of the salts: $[Pb(C_3H_5O_2)_2Pb](ClO_4)_2,2H_2O$ and $[Pb(C_3H_5O_2)_2Pb](BrO_3)_2,4H_2O$. Attempts to obtain similar propionato compounds from the crystalline barium propionate were unsuccessful. H. W.

Pyrogenic Decomposition, at High Temperatures, of Acetic Anhydride. (MLLE.) E. PEYTRAL (*Bull. Soc. chim.*, 1924, [iv], **35**, 969—974; cf. A., 1922, i, 219).—The sudden decomposition of acetic anhydride when rapidly passed through a platinum tube at high temperatures yields as primary products keten and acetic acid, the decomposition involving the least deformation of the molecule. The keten undergoes secondary decomposition into ethylene and carbon monoxide, whilst the acetic acid by secondary decomposition gives methane and carbon dioxide. Small amounts of acetylene and hydrogen are formed, partly by decomposition of the ethylene, but also, especially as the velocity of flow of the acetic anhydride vapour diminishes, by primary decomposition. Hydrogen is also produced, when the velocity of flow is relatively low, by decomposition of the ethylene, giving free carbon or complex hydrocarbons. R. B.

Composition of Soja Bean Oil. E. S. WALLIS and G. H. BURROWS (*J. Amer. Chem. Soc.*, 1924, **46**, 1949—1953).—The fatty acids contained in soja bean oil have been determined by the method of Twitchell (cf. A., 1914, ii, 685; 1917, ii, 428) and the results compared with those obtained in a detailed analysis by Jamieson and Baughmann (cf. A., 1923, i, 281). The percentages of the saturated acids were: palmitic 10, (6·8); stearic 2, (4·4); arachidic 1, (0·7); myristic 0, (—); lignoceric, —, (0·1); the figures in brackets being those of the analytical method. The difference in the distribution between palmitic and stearic acids in the two sets has not been explained. A. C.

Trichloroacrylic Acid and some of its Derivatives. III. Peroxide of Trichloroacrylic Acid. J. Böeseken and H. Gelissen (*Rec. trav. chim.*, 1924, **43**, [v], 266—268).—The *peroxide of trichloroacrylic acid*, $(CCl_2{:}CCl{\cdot}CO)_2O_2$, m. p. 49°, is prepared by the action of hydrogen peroxide and sodium hydroxide on trichloroacrylyl chloride. It is not hydrolysed by water, is sensitive to shock, is very volatile, and attacks the skin. J. K.

Preparation of Dehydracetic Acid from Acetoacetic Ester. F. Arndt and P. Nachtweg.—(See i, 1223.)

Ferric Oxalate and its Application to the Separation of Iron and Calcium. J. Barlot (*Bull. Soc. chim.*, 1924, [iv], **35**, 1026—1030).—Ferric oxalate is obtained as an apparently amorphous, greenish-yellow substance, $Fe_2(C_2O_4)_3,4H_2O$, by the slow evaporation of a solution of ferric hydroxide in saturated oxalic acid solution. Its solution in water is more stable than that in oxalic acid, from which ferrous oxalate slowly separates. It forms stable double salts with other oxalates, and it is proposed to separate iron and calcium by taking advantage of the fact that in the presence of ammonium oxalate and acetic acid, the double calcium ferric oxalate is quantitatively decomposed into soluble ferric ammonium oxalate and insoluble calcium oxalate. S. K. T.

Action of Light on Solutions of Organic Compounds in Chloropicrin. A. Piutti (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 437—438; from *Chem. Zentr.*, 1924, i, 2514; cf. A., 1921, i, 298).—Chloropicrin acts as an oxidising, chlorinating, or nitrating agent, respectively, according to the compound with which it is exposed to light. With acetic acid, oxalic and chloroacetic acids are formed together with chlorine, hydrochloric acid, and nitrous acid. Similarly, with ethyl succinate, succinic acid; with methyl salicylate, methyl chlorosalicylate, oxalic acid, and ammonium tetroxalate; with toluene, benzoic acid, *o*-nitrotoluene, and oxalic acid, and with naphthalene, benzoic and phthalic acids are produced. G. W. R.

Configuration of αα′-Dibromo-dibasic Acids. III. The αα′-Dibromosuccinic Acids. H. R. Ing and W. H. Perkin, jun. (*J. Chem. Soc.*, 1924, **125**, 1814—1830).—Methyl and ethyl esters of *dl*-dibromosuccinic acid described by Pictet and by Michael, but not definitely characterised, have now been obtained in a pure state. Bromination of ethyl maleate gave *ethyl* dl-*dibromosuccinate*, b. p. 137—138°/11 mm. *Methyl* dl-*dibromosuccinate* has m. p. 43°. *Ethyl* meso*dibromosuccinate*, m. p. 58°, and *methyl* meso*dibromosuccinate*, m. p. 65°, were obtained by bromination of the corresponding alkyl fumarates.

Condensation of methyl and ethyl *dl*-dibromosuccinates with the sodium derivative of the corresponding malonic esters gave a yield of 80—90% of the respective *cyclo*propane esters, both of which on hydrolysis yielded dl-cyclo*propane*-1 : 2 : 2 : 3-*tetracarboxylic acid*, dihydrate, m. p. 100°; anhydrous, m. p. 198—200°. d-cyclo*Propane*-1 : 2 : 2 : 3-*tetracarboxylic acid*, m. p. 195—196° (decomp.), $[\alpha]_D^{18}$ +106·5° in water, was obtained by resolving the *dl* isomeride by fractional crystallisation of the brucine salt. The *brucine* salt, $C_7H_6O_8,4C_{23}H_{26}O_4N_2,2H_2O$, has $[\alpha]_D^{18}$ −43·01°. When heated at 200°, the *d* acid is converted into inactive *trans-cyclo*propane-1 : 2 : 3-tricarboxylic acid, m. p. 220°.

Condensation of methyl *meso*dibromosuccinate with methyl sodiomalonate gives methyl-α-carbomethoxytricarballylate, methyl *cyclo*propane-1 : 2 : 2 : 3-tetracarboxylate, and methyl ethanetetracarboxylate. By condensation of ethyl *dl*-dibromosuccinate and ethyl sodiocyanoacetate, a 90% yield of *ethyl* 2-*cyanocyclopropane*-1 : 2 : 3-*tricarboxylate*, b. p. 200—205°/8 mm., was obtained; this gave on hydrolysis *dl-cyclo*propanetetracarboxylic acid. The main product from ethyl *meso*dibromosuccinic acid and ethyl sodiocyanoacetate was methyl α-cyanotricarballylate.

Ethyl *dl*-dibromosuccinate reacts in the cold with ethyl sodiobenzoylacetate to give ethyl 5-phenyl-2 : 3-dihydrofuran-2 : 3 : 4-tricarboxylate, b. p. 227—230°/12 mm., which on hydrolysis yields *α-hydroxy-γ-benzoyltricarballylic acid*,

$$CO_2H\cdot CHBz\cdot CH(CO_2H)\cdot CH(OH)\cdot CO_2H,$$

m. p. 142—143° (decomp.); this acid, when heated above its melting point, is converted into 5-*phenyl*-2 : 3-*dihydrofuran*-2 : 3-*dicarboxylic acid*, m. p. 182—183°, which by repeated crystallisation from boiling water is converted into α-phenacyl-β-hydroxysuccinic acid (phenacylmalic acid), m. p. 175—176°; the latter acid is reconverted into phenyldihydrofurandicarboxylic acid by repeated crystallisation from a mixture of methyl alcohol and chloroform.

Ethyl *meso*-dibromosuccinate and ethyl sodiobenzoylacetate condense to form as main products ethyl dibenzoylsuccinate and *ethyl α-benzoyltricarballylate*, b. p. 220—225°/12 mm.; this when hydrolysed yields phenacylsuccinic acid, m. p. 162—163°. The *oxime* of phenacylsuccinic acid has m. p. 147—148°; the *phenylhydrazone*, m. p. 164—165°.

Condensation of ethyl *dl*-dibromosuccinate with ethyl sodioacetoacetate gives a 95% yield of *ethyl* 5-*methyl*-2 : 3-*dihydrofuran*-2 : 3 : 4-*tricarboxylate*, b. p. 190—195°/18 mm., which yields on hydrolysis acetonylmalic acid, m. p. 150°, and, on treatment with ammonia, an amide, m. p. 195°. Ethyl diacetosuccinate and ethyl α-acetyltricarballylate, m. p. 110°, result from the condensation of ethyl *meso*-dibromosuccinate and ethyl sodioacetoacetate.

C. J. S.

Hydrated Active Tartaric Acid. M. AMADORI (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 507—510).—Crystallisation of aqueous tartaric acid solutions at temperatures below about 5° yields a monohydrated modification, blunt, rhombic prisms, *n* 1·52, *a* : *b* : *c*=0·4706 : 1 : 0·5294. The crystals are stable at temperatures below 5—10°, but at higher temperatures, after turning opaque, they undergo gradual transformation into transparent crystals of ordinary tartaric acid. T. H. P.

Rotatory Dispersion of Derivatives of Tartaric Acid. I. Methylene Derivatives. P. C. Austin and V. A. Carpenter (*J. Chem. Soc.*, 1924, **25**, 1939—1946).—The results obtained for the specific rotation of methylene tartaric acid in aqueous solution at different concentrations and for various wave-lengths can be expressed in one term of Drude's equation. The hydrated and anhydrous acids have m. p. 140·5° and 165°, respectively, and the latter has $[\alpha]_D^{20}$ $-81{\cdot}3°$.

The rotatory dispersion of dimethylene tartrate can also be expressed in one term of Drude's equation, and the specific rotation appears to be independent of the concentration and the solvent. Dimethylene tartrate has m. p. 119°, $[\alpha]_D^{20}$ $+107{\cdot}9°$ in ethyl acetate, and on hydrolysis yields a dibasic acid. C. J. S.

Glutaconic Acids. XVI. Three-carbon Tautomerism in the *cyclo*Propane Series. III. Refractometric Evidence. F. R. Goss, C. K. Ingold, and J. F. Thorpe (*J. Chem. Soc.*, 1924, **125**, 1927—1930).—The authors criticise the conclusions drawn by Auwers and Ottens (this vol., i, 513, 516) from their observations on the exaltations of refractivity exhibited by the esters of the isomeric glutaconic acids, disagree with the view that the isomerism is of geometric character, and consider that the esters belong to the "*cis*" rather than to the "*trans*" type.

Observations of the refractivities of isomeric forms of ethyl 2-methyl-Δ^1-*cyclo*propenedicarboxylate, in which ring formation excludes geometric isomerism, reveal marked exaltations of refractivity, a noteworthy feature being the smaller refractivity of the normal ester. C. J. S.

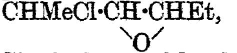
Behaviour of Formaldehyde. A. Ferrini (*Boll. Chim. Farm.*, 1924, **63**, 467—469).—Determination of the ammoniacal nitrogen in hexamethylenetetramine by simple distillation from a solution rendered alkaline by sodium hydroxide or magnesium, calcium, or barium oxide is not possible, only small proportions of ammonia being liberated in this way. Varying amounts of ammonia, always considerably less than the total amount present, are obtained when a mixture of ammonium chloride and the corresponding quantity of formaldehyde is similarly distilled from an alkaline solution, and still lower results are furnished when the ammonium chloride is replaced by ammonia. Addition of metals having a reducing action does not influence the yield of ammonia in any of the above cases. T. H. P.

Reaction between α-Trioxymethylene and Sulphuryl Chloride. K. Fuchs and E. Katscher (*Ber.*, 1924, **57**, [*B*], 1256—1268).—The α-modification of chloroacetic acid, m. p. 56°, is obtained in good yield by heating α-trioxymethylene with sulphuryl chloride and a little zinc chloride at 150—170°. Methyl formate appears to be the primary product of the change, since it is formed in good yield by the action of zinc chloride on α-trioxy methylene at 125°; it is converted by sulphuryl chloride into chloroacetic acid. Higher alkyl formates do not react similarly; thus ethyl formate yields chloral hydrate (cf. Dunlop, T., 1914, **105**, 1155; Hammick and Boeree, T., 1923, **123**, 2881). H. W.

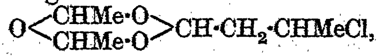
Relationship of Carboligatic Synthesis to Carboxylatic Degradation (Application of Acetaldehyde as Acceptor). C. Neuberg and O. Rosenthal (*Ber.*, 1924, **57**, [*B*], 1436—1441).—The fermentation of pyruvic acid by zymase solution in the presence of dipotassium hydrogen phosphate leads to the formation of acetaldehyde which is partly transformed into acetylmethylcarbinol, CHMeAc·OH. If, under otherwise identical conditions, acetaldehyde is initially added to the solution, the yield of acetylmethylcarbinol is at least doubled, the generated acetaldehyde being "accepted" by the added reagent and utilised in synthetic directions. H. W.

Polymerisation of Halogenated Derivatives of Ethylene Oxide and of Halogenated Aldehydes. B. Helferich and E. Besler (*Ber.*, 1924, **57**, [*B*], 1276—1280).—The tendency of aldehydes towards trimeric polymerisation is considerably increased by the entry of halogen into the molecule; this does not appear to be the case with derivatives of ethylene oxide.

αβ-Dichlorobutaldehyde, b. p. 48—49°/13 mm. (*semicarbazone*, m. p. 96—97°), is converted by an ethereal solution of magnesium ethyl bromide into βγ-*dichloro*-n-*hexan*-δ-*ol*, b. p. 88—93°/12 mm., d_4^{19} 1·1685, n_D^{19} 1·4709, which is transformed by concentrated potassium hydroxide solution into β-*chloro*-γδ-*oxido*-n-*hexane*,


$\underbrace{\mathrm{CHMeCl{\cdot}CH{\cdot}CHEt}}_{\mathrm{O}}$, b. p. 49—50°/13 mm., d_4^{17} 1·0083, n_D^{17} 1·4310. Similarly, dichlorobutaldehyde and magnesium phenyl bromide yield βγ-*dichloro*-α-*phenylbutan*-α-*ol*, b. p. 162—168°/14 mm., d_4^{15} 1·2355, n_D^{15} 1·5500, which is transformed into γ-*chloro*-αβ-*oxido*-α-*phenylbutane*, b. p. 129—131°/15 mm., d_4^{17} 1·1352, n_D^{17} 1·5325. β-*Chloro*-n-*hexan*-δ-*ol*, b. p. 78—79°/13 mm., d_4^{19} 1·0012, n_D^{19} 1·4433, prepared from β-chlorobutaldehyde and magnesium ethyl bromide, is unchanged by aqueous potassium hydroxide solution (50%) at 40—50°. ββγ-*Trichloro*-α-*phenylbutan*-α-*ol*, b. p. 172—173°/13 mm., m. p. 53°, from butylchloral and magnesium phenyl bromide, is decomposed when treated similarly into benzaldehyde and resin.

Halogenated butaldehydes (1 mol.) condense with acetaldehyde (2 mols.) in the presence of hydrogen chloride at 0° to yield hydroxyl-free products which are regarded as mixed paraldehydes. The following individuals are described: *diacet*-β-*chlorobutparaldehyde*,


$\mathrm{O}{<}\begin{matrix}\mathrm{CHMe{\cdot}O}\\ \mathrm{CHMe{\cdot}O}\end{matrix}{>}\mathrm{CH{\cdot}CH_2{\cdot}CHMeCl}$, b. p. 83—85°/13 mm., d_4^{19} 1·0937, n_D^{19} 1·4373; *diacet*-αβ-*dichlorobutparaldehyde*, b. p. 110—112°/14 mm., $d_4^{17·5}$ 1·2227, $n_D^{17·5}$ 1·4604; *diacet*-ααβ-*trichlorobutparaldehyde*, b. p. 118°/13 mm., d_4^{16} 1·3188, n_D^{16} 1·4739; *diacetchloralparaldehyde*, b. p. 97°/13 mm., d_4^{16} 1·3915, n_D^{16} 1·4708.

Monomeric β-*chlorobutaldehyde*, b. p. 28—33°/13 mm., prepared by the addition of the calculated quantity of hydrogen chloride to crotonaldehyde in ethereal solution, passes rapidly into the trimeric form. H. W.

Degradation of Pyridine into Glutacondialdehyde and Re-conversion of the Latter into Pyridine. I. P. Baumgarten (*Ber.*, 1924, **57**, [*B*], 1622—1627).—Pyridine is converted by ethyl chlorosulphonate into an additive compound, which is transformed by aqueous sodium hydroxide into sodium sulphamate and the *sodium* salt of the enolic form of glutacondialdehyde, $ONa{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CHO$. The isolation of the salt in two forms, brownish-red crystals and red leaflets, indicates the existence of the aldehyde also in the cyclic form, $CH{<}\genfrac{}{}{0pt}{}{CH{-}O}{CH{:}CH}{>}CH{\cdot}OH$. The *barium* salt is described. δ-Hydroxy-$\Delta^{\alpha\gamma}$-butadienealdehyde can be preserved unchanged for a short time in ethereal solution, but is too unstable to permit its isolation in substance. The *acetyl* derivative, m. p. 75°, and the *benzoyl* compound, m. p. 116—118°, are described. The latter substance is converted by phenylhydrazine into a *compound*, $C_{18}H_{14}ON_2$, m. p. 149—150°, which has not been identified. As dialdehyde, $CHO{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CHO$, glutacondialdehyde yields an additive *compound*,

$$C_5H_8O_8S_2Na_2,3H_2O,$$

with sodium hydrogen sulphite (2 mols.). It reacts instantly with phenylhydrazine, but the product could not be crystallised; the *p*-bromophenylhydrazine, $C_{17}H_{16}N_4Br_2$, is an amorphous, reddish-brown powder. The sodium salt of the hydroxyaldehyde is converted by boiling aqueous ammonium acetate into pyridine.

H. W.

Purification of Methyl Ethyl Ketone by Sodium Iodide. H. L. Lochte (*Ind. Eng. Chem.*, 1924, **16**, 956).—Methyl ethyl ketone, like acetone (cf. Shipsey and Werner, T., 1898, **103**, 1255), combines with sodium iodide, forming the compound C_4H_8O,NaI. This separates in the crystalline state only when the reagents are slightly moist. It has m. p. 73—74° (decomp., yielding the pure ketone). Commercial samples are best purified by this means.

W. A. S.

Preparation of Higher Ketones. B. Helferich and L. Keiner (*Ber.*, 1924, **57**, [*B*], 1616—1620).—The possibility of preparing higher ketones according to the scheme

$$CH_3{\cdot}C(ONa){:}CR{\cdot}CO_2Et \xrightarrow{R^1{\cdot}COCl} CH_3{\cdot}CO{\cdot}CR(CO{\cdot}R^1){\cdot}CO_2Et \longrightarrow R{\cdot}CH_2{\cdot}CO{\cdot}R^1,$$

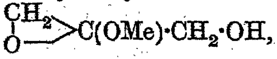
has been examined. The action of acyl chlorides on the sodium salts leads invariably to the production of a mixture of *O*- and *C*-acyl derivatives, the former of which yields the methyl ketone, $CH_3{\cdot}CO{\cdot}CH_2R$, which is obtained also from the alkyl acetoacetate employed. A subsequent separation of the two ketones is therefore essential.

The following acylalkylacetoacetic esters are prepared by dissolving powdered sodium in a solution of the requisite alkylacetoacetic ester in ether and gradually adding the acyl chloride (prepared by means of thionyl chloride) to the ice-cold product: *ethyl* n-*valerylallylacetoacetate*, b. p. 149°/14 mm., $d_4^{16\cdot2}$ 1·0028, n_D^{17} 1·4545; *ethyl* iso*valerylallylacetoacetate*, b. p. 143—144°/14 mm., $d_4^{17\cdot5}$ 0·9998, $n_D^{16\cdot9}$ 1·4546; *ethyl* iso*valerylbenzylacetoacetate*, b. p. 195—196°/14 mm., $d_4^{16\cdot3}$ 1·0524, n_D^{12} 1·5014; *ethyl* Δ^{γ}-*pentenoyl-α-allylacetoacetate*, $CH_3\cdot CO\cdot C(CH_2\cdot CH{:}CH_2)[CO\cdot CH(CH_2\cdot CH{:}CH_2)_2]CO_2Et$, b. p. 169—170°/14 mm., $d_4^{16\cdot6}$ 1·0000, n_D^{16} 1·4739; *ethyl α′-acetoxypropionylallylacetoacetate*, b. p. 167—168°/14 mm., d_4^{21} 1·0950, $n_D^{19\cdot5}$ 1·4590; *ethyl* p-*acetoxybenzoylallylacetoacetate*, b. p. 235°/14 mm.; *ethyl* o-*acetoxybenzoylallylacetoacetate*, b. p. 216—218°/14 mm.; *ethyl* o-*anisoylallylacetoacetate*, b. p. 219°/18 mm., $d_4^{18\cdot0}$ 1·1376, $n_D^{16\cdot9}$ 1·5300. *Ethyl α′-benzoxypropionylallylacetoacetate*, *ethyl trimethylgalloylallylacetoacetate*, and ethyl triacetylgalloylallylacetoacetate could not be distilled without decomposition. For the preparation of *ethyl β-chloropropionylallylacetoacetate*, b. p. 158°/14 mm., d_4^{22} 1·1282, n_D^{22} 1·4710, it is necessary to add the alkylsodioacetoacetate to a solution of β-chloropropionyl chloride in ether.

α-Benzoxypropionyl chloride, prepared from thionyl chloride and the corresponding acid, has m. p. 23—24° after softening at 21°.

The acylalkylacetoacetates are hydrolysed by potassium hydroxide to the following ketones: n-*butyl* Δ^{γ}-*butenyl ketone*, b. p. 72°/14 mm., d_4^{17} 0·8435, n_D^{17} 1·4320 (*semicarbazone*, m. p. 88—89°); iso*butyl* Δ^{γ}-*butenyl ketone*, b. p. 62—63°/14 mm., d_4^{12} 0·8362, $n_D^{12\cdot5}$ 1·4288 (*semicarbazone*, m. p. 101—102° after previous softening); p-*hydroxyphenyl* Δ^{γ}-*butenyl ketone*, b. p. 210—212°/16 mm., m. p. 61·5° after previous softening; o-*methoxyphenyl* Δ^{γ}-*butenyl ketone*, b. p. 152°/16 mm., d_4^{23} 1·0466, n_D^{21} 1·5244; *trimethoxyphenyl* Δ^{γ}-*butenyl ketone*, b. p. 195—196°/14 mm., m. p. 54—55° (*semicarbazone*, m. p. 151° after previous softening); *trihydroxyphenyl* Δ^{γ}-*butenyl ketone*, m. p. 130° after softening at 120° or ($+H_2O$) m. p. 84—85° (*semicarbazone*, m. p. 174—175°). The hydrolysis of ethyl *iso*valerylbenzylacetoacetate, ethyl Δ^{γ}-pentenoylallylacetoacetate, ethyl α′-acetoxy(benzoxy)propionylallylacetoacetates, and of ethyl β′-chloropropionylallylacetoacetates did not lead to the desired ketone.

H. W.

Dihydroxyacetone (II) and a New Method of Preparing Methylglyoxal. H. O. L. FISCHER and C. TAUBE (*Ber.*, 1924, 57, [*B*], 1502—1507).—In continuation of previous work (Fischer and Mildbrand, this vol., i, 613) monomeric dihydroxyacetone has been converted into its *methyl*cyclo*acetal*,  $\begin{matrix}CH_2\\ |\\ O\end{matrix}\!\!>\!C(OMe)\cdot CH_2\cdot OH$, m. p. 90—91°. The *acetate* $(C_7H_{12}O_4)_2$, m. p. 109—110°, and the *toluene*-p-*sulphonate*, $C_{12}H_{16}O_5S$, m. p. 117—118° (decomp.), of the corresponding ethyl*cyclo*acetal are described. *Dihydroxyacetonebenzoylhydrazone*, $CH_2(OH)\cdot C({:}N\cdot NHBz)\cdot CH_2\cdot OH$, m. p. 133°, *dihydroxyacetone*-p-*nitrophenylhydrazone*, m. p. 156°, and *diacetoxyacetone*-p-*nitrophenylhydrazone*, m. p. 138°, have been prepared. Dihydroxyacetone is fermented by certain varieties of bottom yeast, thus giving the first example of a triose which is fermentable without previous spontaneous conversion into a hexose.

Dihydroxyacetone is converted by distillation with phosphoric oxide into pyruvaldehyde, $CH_3{\cdot}CO{\cdot}CHO$, which is unimolecular in the vaporous state but termolecular in the freshly-prepared, dark green liquid form. When preserved during a few hours, the liquid aldehyde becomes converted into a brittle, resinous mass. It yields a *tetraethylacetal*, $CMe(OEt)_2{\cdot}CH(OEt)_2$, b. p. 192°/760 mm., and a *dihydrazone*, m. p. 93—94°. It is converted by methyl chloroformate and potassium cyanide in aqueous solution into *dicarbomethoxymethyltartaronitrile*,

$$CMe(CN)(O{\cdot}CO_2Me){\cdot}CH(O{\cdot}CO_2Me){\cdot}CN,$$

b. p. 100°/0·6 mm., which is hydrolysed by saturated hydrochloric acid at —5° to the corresponding *amide*, m. p. 192°. H. W.

Saturation Relations in Mixtures of Sucrose, Dextrose, and Lævulose. R. F. JACKSON and C. G. SILSBEE (*U.S. Bur. Standards, Tech. Paper* 259, 277—304).—Invert-sugar diminishes the solubility of sucrose in water, and the solubility of dextrose is decreased by the presence of sucrose or lævulose, although the total sugar content is increased. A mixture of sucrose and invert-sugar saturated with respect to both sucrose and dextrose at 30° contains 33·57% of sucrose and 45·44% of invert-sugar, whilst at 50° the proportions are 27·7% and 58%, such solutions possessing the maximum solubilities that can be attained by partly inverted sucrose solutions. Honey is a supersaturated solution of dextrose in presence of lævulose, and its degree of supersaturation can be calculated in terms of the percentages of dextrose, water, and lævulose. C. J. S.

Acetone [*iso*Propylidene] Derivatives of Sugars and their Derivatives. II. Acetone Compounds of Lævulose. H. OHLE and I. KOLLER (*Ber.*, 1924, **57**, [*B*], 1566—1576).—Lævulose is converted by acetone in the presence of anhydrous copper sulphate into α-di*iso*propylidenefructose, βγ-*iso*propylidenefructose, and apparently, α-*iso*propylidenefructose. If sulphuric acid is employed in place of copper sulphate, α-di*iso*propylidenefructose, m. p. 118—119°, is mainly produced with small concentrations of acid; with increasing concentration of the latter, the production of β-di*iso*propylidenefructose becomes more pronounced and this substance becomes the main product when the proportion of acid is 4 c.c. per 100 c.c. of acetone. The preparation of β-di*iso*propylidenefructose is effected more economically when lævulose is replaced by sucrose under otherwise identical conditions, whereby a mixture of β-di*iso*propylidenefructose and di*iso*propylideneglucose is formed which is separated into its components by fractional precipitation of its aqueous solution with 10*N*-sodium hydroxide solution. β-Di*iso*propylidenefructose is readily obtained from inulin by means of sulphuric acid and acetone, whereas these reagents do not affect cellulose, starch, maltose, or lactose. It is similarly produced from α-di*iso*propylidenefructose. It has m. p. 97°, b. p. 110—115°/0·175—0·2 mm., $[\alpha]_D^{22}$ —32·9° in water (c =3·161) $[\alpha]_D^{22}$ —28·98° in benzene, $[\alpha]_D^{21}$ —36·69° in alcohol. It is very much more resistant than the corresponding α-derivative to the hydrolysing action of acids (cf. Irvine and Garrett, T., 1910, **97**, 1277). Mainly for this reason, the authors reject the hypothesis of Irvine and his co-workers (*loc. cit.* and T., 1922, **121**, 2146) that the isomeric di*iso*propylidenefructoses are related to one another in the relation of α- to β-glucoside and consider the second *iso*propylidene residue of the β-derivative to be united to the oxygen atoms, 4 and 5; the position of the oxygen bridge is uncertain. *Methyl*-β-*di*iso*propylidenefructose* has b. p. 90°/0·12 mm., $n_D^{22·5}$ 1·4512, $[\alpha]_D^{26}$ —35·24° in alcohol. The following acyl derivatives of β-di*iso*propylidenefructose are prepared in the presence of a large excess of pyridine: *acetate*, m. p. 66°, $[\alpha]_D^{25}$ —36·02° in alcoholic solution; *benzoate*, long, thin prisms or coarse, poly-sided crystals, m. p. 81°, $[\alpha]_D^{23}$ —21·8° in alcohol; p-*toluenesulphonate*, m. p. 83°, $[\alpha]_D^{19}$ —27·1° in alcohol.

Since the same product is obtained from dextrose by the action of sulphuric acid in amount varying from 1 to 4 c.c. and acetone (100 c.c.) and its nature is independent of the use of α- or β-glucose as initial material, it appears that di*iso*propylideneglucose is a homogeneous product (contrast Irvine and Patterson, T., 1922, **121**, 2146). This view is confirmed by the observation that di*iso*propylideneglucose under the action of sulphuric acid and acetone is, in part, unchanged and in part transformed into *iso*propylideneglucose without any indication of the production of an isomeride. H. W.

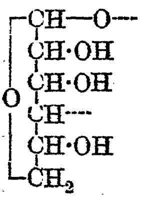
Reversion Synthesis. I. Action of Yeast Maltase. H. PRINGSHEIM and J. LEIBOWITZ (*Ber.*, 1924, **57**, [*B*], 1576—1579).—A solution of dextrose (40%) is subjected to the action of yeast maltase at 37° during four weeks, the optimal hydrogen-ion concentration, p_H =6·4, being used. After fermentation of the residual dextrose by *Saccharomyces Marxianus*, maltose is isolated in the crystalline condition from the portion of the residue soluble in alcohol, whereas slightly impure revertose is obtained from the portion insoluble in alcohol (cf. Croft Hill, T., 1898, **73**, 634; 1903, **83**, 578). The quantity of revertose is much smaller than that of maltose, whereas the reverse is the case in Croft Hill's experiments. H. W.

Products of the Enzymic Fission of Starch. K. SJÖBERG (*Ber.*, 1924, **57**, [*B*], 1251—1256).—The action of undialysed malt amylase solution on amylose followed by precipitation of the product with alcohol (80%) leads to the isolation of a dihexosan, $[\alpha]_{\text{Hg yellow}}^{18}$ +154·5 to 155·7° in water, probably identical with the product described by Pringsheim and Wolfsohn (this vol., i, 714), which readily yields *dihexosan hexa-acetate*, m. p. 150—165°, $[\alpha]_{\text{Hg yellow}}^{18}$ +124·6° in acetic anhydride, $[\alpha]_{\text{Hg yellow}}^{18}$ +123·5° in pyridine, but is only converted by methyl iodide and silver oxide into *tetramethyldihexosan*, $[\alpha]_{\text{Hg yellow}}^{18}$ +144·9°, from which βγ-dimethylglucose is obtained on hydrolysis. Amylopectin, when similarly treated, yields a trihexosan, $[\alpha]_{\text{Hg yellow}}^{18}$ +162·9 to 164·0° in water, probably identical with the compound prepared by Pictet and Jahn (A., 1922, i 987) by heating potato starch in glycerol at 200—210°; the corresponding nona-acetate has m. p. 156—165°, $[\alpha]_{\text{Hg yellow}}^{18}$ +131·4° in acetic anhydride, $[\alpha]_{\text{Hg yellow}}^{18}$ +132·9° in pyridine. H. W.

Starch. XI. Halogen Compounds of the Polyamyloses. H. PRINGSHEIM and A. STEINGROEVER (*Ber.*, 1924, **57**, [*B*], 1579—1581).—Re-examination of the additive compounds of bromine with the polyamyloses (cf. Pringsheim and Eissler, A., 1913, i, 1156; 1915, i, 382) shows them to contain combined in addition to free bromine, so that in this respect they resemble the starch iodides (this vol., i, 618, 837). It does not, however, appear possible to establish a relationship between free and total halogen in the polyamyloses or to detect in their ash an amount of base corresponding with the amount of combined halogen. Bromo-α-hexa-amylose has approximately the composition $(C_6H_{10}O_5)_6Br_2$. Triamylose combines with about 2% more bromine than does hexa-amylose. H. W.

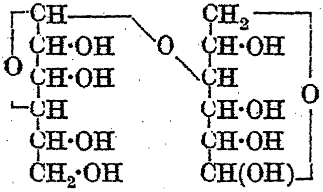
Starch. XII. Constitution of Starch, Glycogen, and Lichen Starch. H. PRINGSHEIM [with A. BEISER, K. WOLFSOHN, L. LEIBOWITZ, and W. KUSENACK] (*Ber.*, 1924, **57**, [*B*], 1581—1598).—Further evidence of the difference in constitution of the content- and integument-substances of the starch granule (cf. this vol., i, 714) is afforded by the observation that the former is converted by cold, concentrated hydrochloric acid into *amylobiose*, $C_{12}H_{22}O_{11}$, $[\alpha]_D^{20}$ +110·9° in aqueous solution, whereas the latter yields *amylotriose*, $C_{18}H_{32}O_{16}$, $[\alpha]_D^{20}$ +124·5° in water (*osazone*, decomp. 142—145°). Under the influence of amylases, amylose is quantitatively converted into maltose, whereas reaction ceases when 65% of amylopectin has been transformed into this sugar; the unattacked residue is identified as trihexosan which, since it can be further fermented with undialysed malt extract, appears to be, not an essential component of the amylopectin molecule, but an accidental residue. The two components occur separately in nature, since amylose is shown to be identical with *iso*lichenin (Pringsheim and Kusenack, this vol., i, 1144) obtained from Iceland moss, which is fermented quantitatively to maltose by fresh malt extract, transformed when heated in glycerol at 185—190° into dihexosan, and hydrolysed by cold, concentrated hydrochloric acid to amylobiose. Amylopectin is identified with glycogen, which is transformed by cold, concentrated hydrochloric acid into amylotriose. The identity of the disaccharide obtained from α-tetra- and β-hexa-amylose and hydrochloric acid (Pringsheim and Leibowitz, this vol., i, 714) with amylobiose is also established.

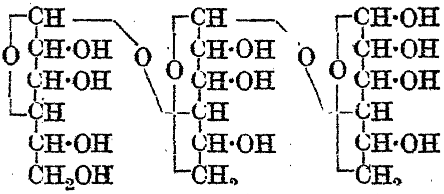
The two-enzyme theory of the amylases (Pringsheim, "Die Polysaccharide," 1923, p. 141) renders account of the liquefaction, caused by fermentative fission of electrolyte, and of the saccharification which can be distinguished by the poisoning of malt amylase. A third type of action, consisting in the depolymerisation of the starch molecule to the non-reducing hexosans, appears to take place intermediately. Since the action consists in the rupture of the amylobiose linking, the enzyme complex is termed amylobiase.


(I.)

Amylobiose, amylotriose, and di- and tri-hexosans are converted quantitatively by malt amylase into maltose; the experimental work is complicated by the unexpected observation that maltose in 1% solution at 37° is slowly converted into dextrose at the acidity (p_{H} 4·5) which is optimal for malt amylase. They are not attacked by the α-glucosidic maltase or the β-glucosidic enzyme of emulsin. The surprising fermentative production of a biose from a different biose or a triose, which has nothing in common with the reversible, synthetic action of enzymes, is most readily explained by the hypothesis that a glucose residue (1), probably as a consequence of the nature of its oxygen bridge, is eliminated as a radical which unites with another similar group to yield maltose.

The quantitative formation of maltose from amylobiose renders the formula proposed previously (Pringsheim and Leibowitz, (*loc. cit.*) untenable. The following constitutions are proposed for amylobiose and amylotriose:


Amylobiose.


Amylotriose.

It is suggested that the formaldehyde formed during the assimilation of carbon dioxide by plants passes immediately into the author's radical, from which the content- and integument-substances of the starch granule are produced directly. H. W.

Carbonic Esters of Cellulose. E. HEUSER and F. SCHNEIDER (*Ber.*, 1924, **57**, [*B*], 1389—1392).—The action of an excess of methyl chloroformate on a solution of hydrocellulose in cold aqueous sodium hydroxide (8%) gives *esters* which approximate very closely to the formula $C_6H_8O_3(O{\cdot}CO_2Me)_2$. They form a white, amorphous, granular material, soluble in pyridine, chloroform, and acetic acid. They are readily hydrolysed. Analysis of them is effected by determining carbon dioxide and methoxyl content. H. W.

Mannan Content of Wood-cellulose and its Analytical Determination. E. HEUSER and W. DAMMEL (*Cellulosechem.*, 1924, **5**, 45—53).—The mannan in the cellulose from coniferous woods is determined by Schorger's method (*J. Ind. Eng. Chem.*, 1917, **9**, 748) after hydrolysis with hydrochloric acid by precipitation in the form of mannose bromophenylhydrazone. Mannan is extracted by treating the pulp with 17% aqueous sodium hydroxide, but the exhaustion is not always complete even after two or three treatments. It is determined after hydrolysis of the extract, but Schorger's method by direct hydrolysis of the pulp is to be preferred.

On acidification of the alkaline extract and precipitation with alcohol, a portion of the mannan is found in the precipitated hemicellulose, but a further portion remains in the filtrate. The pentosans behave in a similar manner, being distributed in unequal porportions in the α-, β-, and γ-cellulose fractions. There is no support for the suggestion that the mannose forms an integral component of the wood cellulose molecule. The statement of Lenze, Pleus, and Müller (*J. pr. Chem.*, 1922, **101**, 213) that when the β-cellulose from wood pulp is boiled with 4% nitric acid, the hemicelluloses are completely hydrolysed, leaving a residue of oxycellulose, is not accepted as the basis of a valid method for the determination of oxycellulose in wood pulp. In the first place, the oxycellulose is not quantitatively present in the β-cellulose fraction, and, secondly, the hydrolysis is not quantitatively selective. The phenylhydrazone indicated by those authors as that of methylfurfuraldehyde is proved to be that of hydroxymethylfurfuraldehyde derived from dextrose. J. F. B.

Action of Liquid Ammonia and Sodamide on Halogen Derivatives of Ethane. Preparation of Pure Monoethylamine. PICON (*Bull. Soc. chim.*, 1924, [iv], **35**, 979—981).—Liquid ammonia does not appreciably react with ethyl chloride even at the ordinary temperature. With ethyl bromide or iodide, reaction takes place at —40°, more rapidly at the ordinary temperature, yielding a mixture of the primary and secondary amine in approximately equal amounts. The reaction between sodamide and potassium ethyl sulphate (Titherley, T., 1901, **79**, 391) gives very poor yields of ethylamine, owing to the large quantity of ethylene and ammonia produced. In the presence of liquid ammonia, at the ordinary temperature, sodamide yields a mixture of primary, secondary, and tertiary amine with ethyl bromide or iodide, some ethylene being also formed, but with ethyl chloride pure ethylamine is obtained. The yield amounts to only 30% of the theoretical, owing to the formation of a considerable quantity of ethylene. R. B.

Mechanism of Oxidation Processes. VIII. Scission by Oxidation of Amino-acids. H. WIELAND and F. BERGEL (*Annalen*, 1924, **439**, 196—210; cf. this vol., i, 606).—Glycine, alanine, and phenylalanine are oxidised by gaseous oxygen in presence of active charcoal at 38° to carbon dioxide, ammonia (in equimolecular proportions), an aldehyde with one carbon atom less than the original acid, and a little of the corresponding acid. Aspartic acid gives 2 mols. of carbon dioxide to 1 mol. of ammonia. α-Iminopropionic acid gives carbon dioxide, ammonia, and acetaldehyde; α-amino*iso*butyric acid is unaffected. The free oxygen may be replaced by alloxan, *m*-dinitrobenzene, dithioglycollic acid, or *p*-benzoquinone. Succinic acid is dehydrogenated by dithioglycollic acid in presence of freshly-minced liver. These experimental results provide new material for an exhaustive discussion of the mechanism involved in the disruption of α-amino-acids. W. A. S.

Steric Series. IV. Configuration of Alanine. K. Freudenberg and F. Rhino (*Ber.*, 1924, **57**, [*B*], 1547—1557; cf. A., 1923, i, 215).—Basing the work on the hypothesis that analogous compounds of like configuration suffer corresponding changes in optical rotation under similar conditions (cf. Clough, T., 1918, **113**, 526), an examination of lactic acid and alanine has been made. To obtain constants free from external influences it is necessary to avoid the presence of free hydroxy, carboxy, or amino groups and to determine the rotations of the liquid or molten substances. Where this is impossible, the rotation is obtained by extrapolation from a series of solutions of different and ultimately very high concentration. In cases of doubt, several solvents are employed, the choice falling on those in which the rotation of the dissolved substance is least dependent on the concentration. The elimination of the use of a solvent is the most important feature of the whole problem, since variations in rotation due to solvent are of very much greater magnitude than those due to temperature. The abnormalities due to rotatory dispersion also become less in evidence. The measurements are effected for light of four different wave-lengths. Comparison of the different compounds with one another is based on the values of K_M deduced from the equation

$$(\lambda_n^2-\lambda_0^2)\,.\,[M]_n=K_M,$$

where M is the molecular rotation (cf. Rupe and Ackermann, A., 1920, ii, 652). It is thus established that *l*-lactic acid has the same configuration as natural *d*-alanine. From the point of view of the Walden inversion, the action of nitrous acid on alanine, serine, and aspartic acid occurs, therefore, without inversion, since these compounds yield hydroxy-acids belonging to the *l*-series.

The following compounds are incidentally described; the specific rotations are recorded for the wave-lengths 649, 578, 546, and 444 μμ: *ethyl* d-*α-acetoxypropionate*, b. p. 170—172°/760 mm.; *ethyl* r-*α-hexahydrobenzoxypropionate*, b. p. 132—135°/13 mm., and the corresponding d-*ester*; methyl r-*α-benzoxypropionate*, b. p. 144—145°/13 mm., 275—280°/760 mm., and the corresponding *ethyl* ester, b. p. 150°/12 mm., 282°/760 mm., and the similar d-*compounds*. *r*-α-Benzoxypropionamide, m. p. 116—117°; *methyl* r-p-*toluenesulphonoxypropionate*, b. p. 170—173°/0·5 mm.; *ethyl* d-p-*toluenesulphonoxypropionate*, b. p. 175—177°/0·5 mm.; *ethyl* r-p-*toluenesulphonoxypropionate*, b. p. 175—177°/0·5 mm.; r-*α*-p-*toluenesulphonoxypropionamide*, m. p. 87—88°, and the corresponding d-*amide*, m. p. 105°; ethyl *dl*-α-acetamidopropionate, m. p. 39°, and the corresponding *l*-ester, m. p. 34—35°; *ethyl* r-*α-hexahydrobenzamidopropionate*, from the components in the presence of pyridine, m. p. 77—78°; *ethyl* l-*α-hexahydrobenzamidopropionate*, m. p. 75°; *methyl* l-*α-benzoylaminopropionate*, m. p. 58°; *ethyl* l-*α-benzamidopropionate*, m. p. 97—98°; l-*α-benzamidopropionamide*, m. p. 228—229°; l-*α*-p-*toluenesulphonamidopropionamide*, m. p. 212—213°; *ethyl* l-*α*-p-*toluenesulphonamidopropionate*. H. W.

Preparation of Melanins containing Sulphur. O. Adler (*Biochem. Z.*, 1924, **148**, 541—547).—Using the method already described (A., 1923, i, 591, 1218), *tyrosinesulphomelanic acid*, a dark grey, hygroscopic, amorphous powder, has been prepared from tyrosinesulphonic acid. The *sodium* and *barium* salts are described. By heating at 270° for 2 hours, the acid is converted into *tyrosinesulphomelanin*, a black, hygroscopic powder. Similarly, from thiophen, *thiophenmelanic acid*, a dark, amorphous powder, and *thiophenemelanin*, a black powder, were obtained.

J. P.

Action of Triphenylmethyl Chloride on Ethyl β-Aminocrotonate and Analogous Compounds. E. Benary and P. Lorth.—(See i, 1192.)

Complexes of Carbamide with Cadmium Salts. L. Belladen and A. Ciampa (*Gazzetta*, 1924, **54**, 568—571).—The following complex *compounds* are described: $CdCl_2,CO(NH_2)_2$; $CdCl_2,2CO(NH_2)_2$; $CdBr_2,CO(NH_2)_2$ and $CdBr_2,2CO(NH_2)_2$; $CdI_2,CO(NH_2)_2$ and $CdI_2,2CO(NH_2)_2$; $Cd(ClO_4)_2,6CO(NH_2)_2$; $Cd(SCN)_2,2CO(NH_2)_2$. The results of cryoscopic and conductivity measurements show that, in aqueous solution, these complex compounds undergo complete dissociation into their components.

T. H. P.

Electrolysis of Aqueous Solutions of Cyanamide. N. Kameyama (*J. Coll. Eng. Tokyo*, 1924, **13**, 271—310).—The electrolytic oxidation and reduction of aqueous solutions of cyanamide, acidified with sulphuric acid, sodium acetate, and acetic acid, in the presence of potassium sulphate, and, in the case of oxidation, in alkaline solution, and of solutions of acid calcium cyanamide, $Ca(CN_2H)_2$, using lead, mercury, cadmium, zinc, and platinum cathodes, was studied at the ordinary or a slightly elevated temperature. Electrolytic reduction follows the same course as that produced by nascent hydrogen, methylamine and ammonia being produced. The intermediate formation of hydrogen cyanide could not be detected. The highest current efficiencies obtained were 10—20% with the cadmium cathode in the cyanamide solution containing sodium acetate and acetic acid or in the acid calcium cyanamide solution. Electrolysis of cyanamide solution without the separation of anodic and cathodic compartments yielded a trace of cyanide in acidic or neutral solutions, and a larger quantity, together with some cyanate, in alkaline solutions. On anodic oxidation, using a Pukall diaphragm and a platinum anode, the cyanamide solution became first yellow, then reddish-orange, and at this stage, on standing over-night, the solution deposited an orange-red, crystalline compound containing nitrogen. On continued electrolysis, the solution became pale yellow again and finally colourless. Electrolysis of the cyanamide in alkaline solution without a diaphragm yielded cyanide. Preliminary experiments on the anodic oxidation of cyanamide in alkaline solution showed the production of cyanate in solution and the evolution of nitrogen.

J. W. B.

Conversion of Calcium Cyanamide into Cyanides. J. DODONOW (*Ann. Inst. agron. Saratow*, 1922, **1**, 1–13; from *Chem. Zentr.*, 1924, ii, 317–318).—When a mixture of calcium cyanamide (160 g.), sodium carbonate (125 g.), and wood charcoal (32 g.) was added gradually to 20 g. of sodium carbonate heated to bright redness, and the temperature maintained for 20 mins., 63·5 g. of sodium cyanide (78% yield on the nitrogen of the cyanamide) were obtained; with potassium carbonate the yield was 70%. By heating calcium cyanamide with excess of water at 60°, dicyanodiamide was produced in 82% yield, together with carbamide (7%); boiling with water gave a 60% yield.

Hydrazidicarbonazide and its Formation as By-product of the Diazotisation of Carbohydrazide. W. KESTING (*Ber.*, 1924, **57**, [*B*], 1321—1324).—The addition of hydrochloric acid to an aqueous solution of carbohydrazide and sodium nitrite in the presence of light petroleum, b. p. 98°, leads to the formation of carboazide, $CO(N_3)_2$, which passes into the light petroleum, and hydrazidicarbonazide, $N_2H_2(CO\cdot N_3)_2$, which remains in the aqueous layer (cf. Stollé and Krauch, A., 1914, i, 592). The latter substance, m. p. 150—152° (decomp.) when slowly heated, is highly explosive. With piperidine, *hydrazidicarbonpiperidide*, $N_2H_2(CO\cdot NC_5H_{10})_2$, m. p. 179°, is formed. H. W.

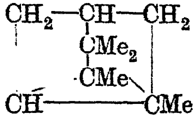
Action of Ammonium Hydroxide on Copper Ferrocyanide. E. D. CRITTENDEN (*J. Amer. Chem. Soc.*, 1924, **46**, 1210—1211).—Copper ferrocyanide does not dissolve in ammonia solution, but forms a silky, brown solid which probably has the formula $Cu_2Fe(CN)_6,4NH_3$. The presence of a trace of ammonia seriously impairs the delicacy of the ferrocyanide test for small quantities of copper. M. S. B.

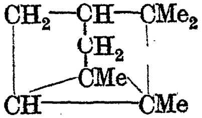
Nitrogenous Condensation Products from Acetylene and Ammonia. CHEM. FABR. RHENANIA (D.R.-P. 382091; from *Chem. Zentr.*, 1924, i, 2298—2399).—Acetylene and ammonia react in the presence of water vapour and a hydrated substance, such as aluminium hydroxide, forming under different conditions acetonitrile, picoline, aldehyde-ammonia, ethylamine, and nitrogenous bases of high molecular weight. The principal product is acetonitrile. G. W. R.

Application of Zelinsky's Method of Catalytic Dehydrogenation to the Detection of Decahydronaphthalenes in Low-temperature Tar. H. KAFFER (*Ber.*, 1924, **57**, [*B*], 1261—1265).—Suitable fractions of low-temperature tar are freed from aromatic hydrocarbons by treatment with sulphuric acid and dehydrogenated by repeated passage at 320—330° over platinised charcoal which has been activated by contact with oxygen at the atmospheric temperature. The products are treated with sulphuric acid and the sulphonic acids are decomposed into the corresponding hydrocarbons by means of superheated steam. Naphthalene, 1-methyl- and 1 : 6-dimethyl-naphthalene are thereby isolated, thus establishing the presence of the corresponding decahydro compounds in the tar. Activated platinised charcoal is a more active catalyst than platinised asbestos. H. W.

Methylcyclene. S. NAMETKIN and L. BRÜSSOFF (*Ber.*, 1924, **57**, [*B*], 1258—1260).—6-Methylcamphor is converted by hydrazine hydrate at 180—190° into a mixture of the corresponding *hydrazone*, b. p. 153—154°/42 mm., m. p. 103—105°, and *azine*, m. p. 131—133°. The hydrazone is oxidised by mercuric oxide to *methylcyclene* (I or II), b. p. 168—168·5°/762 mm., m. p. 110·5—111°.

(I.)





(II.)

The new hydrocarbon is not identical with the product of the dehydration of *tert.*-methylfenchol or *tert.*-methylborneol (Bredt, A., 1919, i, 125). H. W.

Hydrolysis of the *p*-Toluenesulphonchloroamides in Water. F. G. SOPER (*J. Chem. Soc.*, 1924, **125**, 1899—1910).—In aqueous solution, *p*-toluenesulphondichloroamide is hydrolysed into hypochlorous acid (cf. Selivanov, A., 1893, i, 192) and the monochloroamide: $C_7H_7\cdot SO_2\cdot NCl_2 + H_2O \rightleftharpoons C_7H_7\cdot SO_2\cdot NHCl + HOCl$, the existence of the latter, which could not be isolated, being indicated by the greater solubility of the dichloroamide in solutions of the sulphonamide than in water. The monochloroamide probably exists as an equilibrium mixture of the two isomerides,

$$C_7H_7\cdot SO_2\cdot NHCl$$

and $C_7H_7\cdot SO_2H{:}NCl$, hydrolysis of the monochloroamide from equimolecular quantities of the sulphonamide and hypochlorous acid and from acidification of "chloramine-T" (sodium salt of the monochloroamide), yielding identical results. From determinations of the solubility of the dichloroamide in solutions of the sulphonamide (cf. Löwenherz, A., 1898, ii, 326) and of the free chlorine in solutions of "chloramine-T" acidified with hydrochloric acid (cf. Orton and Jones, T., 1909, **95**, 1456) the equilibrium constants of the hydrolysis of mono- and di-chloroamides of *p*-toluenesulphonamide in water at 25° have been calculated as $4{\cdot}9 \times 10^{-8}$ and $8{\cdot}0 \times 10^{-7}$, respectively. The concentration of hypochlorous acid in solutions of acidified "chloramine-T" is independent of the concentration of the "chloramine-T." R. B.

Nitro-*p*-*tert.*-butyltoluene. M. BATTEGAY and P. HAEFFELY (*Bull. Soc. chim.*, 1924, [iv], **35**, 981—988).—Nitration of *p*-*tert.*-butyltoluene with nitric and sulphuric acids at 5—10° gives *2-nitro-*p*-tert.-butyltoluene*, a yellow oil, volatile in steam, b. p. 138—139°/13 mm., having a slight odour of musk. Its constitution is proved by the following series of reactions. On oxidation in pyridine with potassium permanganate it gives o-*nitro*-p-tert.-*butylbenzoic acid*, m. p. 145°, which on reduction in dilute ammonia with ferrous sulphate yields o-*amino*-p-tert.-*butylbenzoic acid*, m. p. 174°. The amino-acid, by treatment with potassium cyanide and formaldehyde in benzene suspension, followed by hydrolysis with sodium hydroxide, is converted into p-tert.-*butylphenylglycine*-o-*carboxylic acid*, m. p. 246°, and the sodium salt of the glycinecarboxylic acid on fusion with sodium and potassium hydroxides at 270° yields 6 : 6′-*dibutylindigotin*, violet needles, a reaction which proves the position of the nitro-group. On reduction, 2-nitro-*p-tert.*-butyltoluene yields p-tert.-*butyl*-o-*toluidine*, b. p. 128—129°/13 mm., volatile in steam (*hydrochloride*; *acetyl* derivative, m. p. 112°; *benzoyl* derivative, m. p. 143°; *toluene*-p-*sulphonyl* derivative, m. p. 158°), converted by the diazo reaction into p-tert.-*butyl*-o-*cresol*, a viscous oil, which on treatment with nitrous acid gives, besides traces of a nitrogenous substance, m. p. 172°, p-tert.-*butyltoluquinone*, golden-yellow spangles, m. p. 95°, volatile in steam and possessing a powerful quinone-like odour. On further nitration at 30° with fuming nitric and sulphuric acids, 2-nitro-*p-tert.*-butyltoluene gives, in 90% of the theoretical yield, the 2 : 6-dinitro-*p-tert.*-butyltoluene, m. p. 94—95°, obtained by Bialobrzeski (A., 1897, i, 514), the constitution of which follows from its reduction to p-tert.-*butyl*-2 : 6-*tolylenediamine*. R. B.

Artificial Musks. M. BATTEGAY and M. KAPPELER (*Bull. Soc. chim.*, 1924, [iv], **35**, 989—996).—With a view to obtain evidence as to whether the odour of artificial musk (trinitro-*tert.*-butyl-*m*-xylene) is due to the specific influence of the tertiary butyl group as such or merely to the tertiary carbon atom which it contains, a number of analogous derivatives of *m*-xylene have been prepared and the properties of their nitro derivatives examined. Replacement of the *tert.*-butyl group by *cyclo*hexyl leads to an odourless trinitro compound; *tert.*-heptyl-*m*-xylene (*m*-xylyltriethylmethane) yields a nitration product with a strong but somewhat disagreeable odour of musk, whilst 5-triphenylmethyl-*m*-xylene yields only odourless nitration products, and it is concluded that both the tertiary carbon atom and the butyl radical as such exert an "osmophoric" influence.

m-Xylene and *cyclo*hexyl bromide condense in the presence of ferric or aluminium chloride, yielding a *di*cyclo*hexyl*-m-*xylene*, $C_{20}H_{30}$, m. p. 104°, and 5-cyclo*hexyl*-m-*xylene*, b. p. 265—266°/748 mm., 142—143°/17 mm., with an odour of geranium, which on nitration with nitric and fuming sulphuric acids gives 2 : 4 : 6-*trinitro*-5-cyclo*hexyl*-m-*xylene*, m. p. 117—118°, the constitution of which follows from its synthesis by nitrating the hydrocarbon obtained by deaminating the condensation product of *cyclo*hexyl bromide and 2-*m*-xylidine hydrochloride. Similarly, *m*-xylene and methyldiethylethylene (Saytzeff, A., 1898, i, 289) in the presence of aluminium chloride readily yield 5-*αα-diethylpropyl*-m-*xylene*, b. p. 257—259°/745 mm., which on nitration with nitric and sulphuric acids yields only trinitro-*m*-xylene, whilst with nitric acid and acetic anhydride an oily product of musk-like odour is obtained. Triphenylcarbinol and 2-*m*-xylidine hydrochloride in boiling acetic acid yield 5-*triphenylmethyl*-2-m-*xylidine hydrochloride*, a red powder, m. p. 277—278°; the free *base* has m. p. 177°. On diazotisation of the sulphate in acetic acid solution with amyl nitrite and decomposition of the *diazonium* salt with absolute alcohol in the presence of copper, 5-*triphenylmethyl*-m-*xylene*, m. p. 154°, b. p. 450°, is obtained. No definite nitration product was obtained. R. B.

Sulpho Derivatives of Acenaphthene. K. Dziewoński and T. Stolyhwo (*Ber.*, 1924, **57**, [*B*], 1531—1540).—Acenaphthene-5-sulphonic acid (cf. Oliveri-Mandala, *Rend. Accad. Lincei*, 1912, 779) is conveniently prepared by the action of sulphuric acid (8 g.) on acenaphthene (10 g.) at 100°, and is readily separated as the sodium salt; the ethyl ester, m. p. 87—88°, and the *amide*, m. p. 196—199°, are described. The sodium salt is transformed when heated with potassium ferrocyanide, potassium cyanide, or potassium hydroxide into acenaphthylene and polyacenaphthylene. Acenaphthene-3-sulphonic acid (described erroneously in D.R.-P. 248994 as the 1-sulphonic acid because of its conversion by fused potassium hydroxide into acenaphthylene) is obtained by the addition of sulphuric acid (100%) or chlorosulphonic acid to a solution of acenaphthene in nitrobenzene at 0—20°. The *sodium* and *barium* salts are described. *Acenaphthene*-3-*sulphonyl chloride* is readily converted into *acenaphthene*-3-*sulphonamide*, m. p. 222—223°, and *ethyl acenaphthene*-3-*sulphonate*, m. p. 137—139°. Attempts to prepare the corresponding nitrile from the sulphonate yielded only acenaphthylene and its polymeride. The constitution of the acid is established by its oxidation with sodium dichromate in glacial acetic acid solution to 2-sulphonaphthalene-1 : 8-dicarboxylic acid (the *sodium hydrogen* salt and the *barium* salt are described); the acid is converted by fused potassium hydroxide into 2-naphthol-1 : 8-dicarboxylic acid (cf. Dziewoński and Stolyhwo, this vol., i, 1199).

Treatment of acenaphthene with an excess of concentrated or with fuming sulphuric acid leads to the formation of disulphonic acids of which two, termed provisionally α- and β-acid, have been isolated. In contrast to the monosulphonic acids they yield barium salts which dissolve very freely in water and are adapted to their isolation. *Acenaphthene*-α-*disulphonic* acid is prepared from the hydrocarbon (10 g.) and concentrated sulphuric acid (20 g.) at 100°; the *sodium* and *barium* salts and the *disulphonyl chloride* are described. *Acenaphthene*-α-*disulphonamide* and *methyl acenaphthene*-α-*disulphonate* have m. p. 282° (decomp.) and 170—171°, respectively. The acid is readily nitrated to a nitroacenaphthene-α-disulphonic acid which is isolated as the *sodium* salt. Acenaphthene (10 g.) is converted by cold concentrated sulphuric acid (50 g.) into acenaphthene-β-disulphonic acid [*barium* and *sodium* salts; *sulphonyl chloride*; *acenaphthene*-β-*disulphonamide*, m. p. 301° (decomp.)]. Desulphonation of either acenaphthenedisulphonic acid gives primarily acenaphthene-5-monosulphonic acid and ultimately acenaphthene; in each case one of the two sulphonic groups must occupy position 5. H. W.

Complex Isomerism. E. Hertel (*Ber.*, 1924, **57**, [*B*], 1559—1561).—o-*Bromoaniline picrate* exists in two forms, long, red needles, m. p. 128·5°, obtained by allowing a solution of the components in chlorobenzene to crystallise above 95°, and a yellow variety prepared in alcoholic solution. It therefore appears to fulfil the predictions of Pfeiffer ("Organische Molekülverbindungen," 1922, p. 226) with regard to the existence of two types of picrate, in one of which the hydroxylic hydrogen of picric acid is united by a subsidiary valency to the basic nitrogen atom ("true picrates"), whereas in the other the subsidiary valency of the nitro group of picric acid is saturated by the valency field produced by the residual affinities of the aromatic nucleus of the base, $OH\cdot C_6H_2(NO_2)_3 \ldots RNH_2$. When picric acid is triturated with *o*-bromoaniline, a carmine-red mixture is obtained which becomes yellow slowly at the atmospheric temperature, instantaneously at 65°; a similar, irreversible effect is produced immediately by the vapours of ether, acetone, or ethyl acetate. Analogous observations are made with *o*-bromoaniline and trinitrobenzene. *Picrates* of the following bases are described incidentally: m-*bromoaniline*, m. p. 180°; p-*bromoaniline*, m. p. 180°; o-, m-, and p-*chloroanilines*, m. p. 134°, 177°, and 178°, respectively; 2 : 4-*dichloroaniline*, m. p. 106°; 2 : 4-*dibromoaniline*, m. p. 124°; 2 : 6-*dibromoaniline*, m. p. 123—124° (the molten product solidifies when quickly cooled to a red mass, m. p. 95°); 2 : 4 : 6-*tribromoaniline*. H. W.

Acetoacetanilide. C. Bülow and E. King (*Annalen*, 1924, **439**, 211—220).—α-*Chloroacetoacetanilide*, m. p. 137·5°, is produced by the interaction of sulphuryl chloride and acetoacetanilide in cold ethereal suspension. With excess (3 mols.) of sulphuryl chloride, αα-*dichloroacetoacetanilide*, m. p. 46—47°, is formed, which tends to resinify on standing. By passing chlorine into an ethereal suspension of acetoacetanilide, a dark brown oil is produced which if dissolved in benzene slowly deposits crystals of αα-*dichloroacetoacet*-p-*chloroanilide* in very poor yield, m. p. 63—64°. α-Chloroacetoacetanilide is more stable than acetoacetanilide, being hydrolysed only by dilute hydrochloric acid at 120—130° to chloroacetone, carbon dioxide, and aniline.

β-n-*Butylaminocrotonanilide*, m. p. 98°, from *n*-butylamine and acetoacetanilide, is easily hydrolysed by water or dilute acids. By the interaction of α-chloroacetoacetanilide and alcoholic ammonia, α-*chloro*-β-*aminocrotonanilide*, m. p. 143°, is produced; it is stable on boiling with water, but is hydrolysed by dilute acids; α-*chloro*-β-*methylaminocrotonanilide*, m. p. 96·5°, is similar. α-*Chloro*-β-n-*butylaminocrotonanilide*, m. p. 65°, is very unstable. The interaction of aniline and α-chloroacetoacetanilide yields α : β-*diphenylaminocrotonanilide*, m. p. 201—202°.

β-*Chloro*-α-*hydroxylepidine*, m. p. 276°, is formed by treatment of α-chloroacetoacetanilide with concentrated sulphuric acid; the chlorine atom is very stable. On nitration, it gives a mononitro compound, probably 3-chloro-5-nitro-2-hydroxy-4-methylquinoline, m. p. above 330°.

By coupling α-chloroacetoacetanilide with diazotised aniline, *α-chloroglyoxylanilide phenylhydrazone*, NHPh·N:CCl·CO·NHPh, m. p. 161°, is produced. The chlorine is now easily replaceable, for with alcoholic ammonia, *α-aminoglyoxylanilide phenylhydrazone* is produced, m. p. 152—154°, apt to gelatinise. The *hydrochloride* is unstable, decomp. 150°; m. p. 213° in an atmosphere of dry hydrogen chloride. The corresponding *α-anilinoglyoxylanilide phenylhydrazone* has m. p. 171°. When chlorine is passed at 0° into an alcoholic suspension of α-chloroglyoxylanilide phenylhydrazone, the *2-chloroanilide 2 : 4-dichlorophenylhydrazone*, m. p. 199·5°, is formed; this was also synthesised from acetoacet-2-chloroanilide and 2 : 4-dichlorobenzenediazonium chloride.

α-Chloroglyoxylanilide o-*tolylhydrazone*, from the α-chloroacetoacetanilide and diazotised *o*-toluidine, has m. p. 115°; the p-*tolylhydrazone* has m. p. 175°; the 1 : 3 : *5-xylylhydrazone*, m. p. 135·5°; the 1 : 3 : *4-xylylhydrazone*, m. p. 138°. *α-Chloroglyoxylanilide phenylhydrazone*-o-*carboxylic acid*, from α-chloroacetoacetanilide and diazotised anthranilic acid, has m. p. 216—217° (decomp.). The β-*naphthylhydrazone* melts indistinctly at 183°, and the *α-naphthylhydrazone* at 189—191°. A. E. C.

***iso*Nitriles. VIII. Reaction with Aldehydes or Ketones in Presence of Organic Acids.** M. Passerini (*Gazzetta*, 1924, 54, 529—540).—The reaction of an aldehyde or ketone with an aromatic *iso*nitrile in presence of an organic acid (cf. A., 1921, i, 895) is, with some exceptions, of general application and has now been extended to aliphatic aldehydes and to cases in which the aldehyde or ketone and the acid are derived from different organic radicals. Diketones also undergo this reaction, in which, however, only one of the two ketonic groups takes part. Neither camphor nor santonine reacts in this way. Halogenated ketones, which with water form hydrates, react with phenylcarbylamine in the same manner as the hydrates of halogenated aldehydes react in absence of organic acid (cf. A., 1922, i, 731).

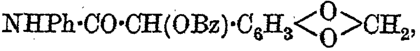
*α-Salicoyloxy*iso*butyranilide*, $\mathrm{NHPh{\cdot}CO{\cdot}CMe_2{\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}OH}$, m. p. 118—119°, obtained from phenylcarbylamine, acetone, and salicylic acid, yields α-hydroxy*iso*butyranilide and salicylic acid on hydrolysis. *β-Chloro-α-benzoyloxy*iso*butyranilide*, $\mathrm{NHPh{\cdot}CO{\cdot}CMe(CH_2Cl){\cdot}OBz}$, from phenylcarbylamine, chloroacetone, and benzoic acid, m. p. 97—99°, yields α-hydroxy-β-chloro*iso*butyranilide and benzoic acid on hydrolysis.

*β-Chloro-α-acetoxy*iso*butyranilide*, $\mathrm{NHPh{\cdot}CO{\cdot}CMe(CH_2Cl){\cdot}OAc}$, from phenylcarbylamine, chloroacetone, and acetic acid, forms a pale yellow syrup and undergoes normal hydrolysis. *α-Acetoxy-α-methylbutyranilide*, NHPh·CO·CMeEt·OAc, m. p. 71°, from phenylcarbylamine, methyl ethyl ketone, and acetic acid, on hydrolysis yields acetic acid and *α-hydroxy-α-methylbutyranilide*, m. p. 114°, which undergoes further hydrolysis to aniline and α-hydroxy-α-methylbutyric acid. *α-Acetyl-lactanilide*,

NHPh·CO·CHMe·OAc,

m. p. 122°, from phenylcarbylamine, acetaldehyde, and acetic acid, gives lactanilide on hydrolysis. *α-Benzoyl-α-benzoyloxy-α-phenylacetanilide*, $\mathrm{NHPh{\cdot}CO{\cdot}CPhBz{\cdot}OBz}$, from phenylcarbylamine, benzil, and acetic acid, m. p. 194—195° (decomp.), yields mandelanilide and benzoic acid on hydrolysis. m-*Nitro-α-benzoylmandelanilide*, $\mathrm{NHPh{\cdot}CO{\cdot}CH(OBz){\cdot}C_6H_4{\cdot}NO_2}$, m. p. 155—157°, from phenylcarbylamine, *m*-nitrobenzaldehyde, and benzoic acid, yields aniline, benzoic acid, and *m*-nitromandelic acid on hydrolysis.

o-*Benzoyl*-4 : 5-*dioxymethylenephenylglycollanilide*,



$$\mathrm{NHPh{\cdot}CO{\cdot}CH(OBz){\cdot}C_6H_3}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}{>}\mathrm{CH_2},$$

m. p. 160°, from phenylcarbylamine, piperonal, and benzoic acid, on hydrolysis, yields benzoic acid and 4 : 5-*dioxymethylenephenyl*-1-*glycollanilide*, m. p. 114°. ββ-*Dichloro-α-hydroxyisobutyranilide*, $\mathrm{NHPh{\cdot}CO{\cdot}CMe(OH){\cdot}CHCl_2}$, m. p. 132—133°, from phenylcarbylamine and *as*.-dichloroacetone hydrate, yields aniline and ββ-dichloro-α-hydroxy*iso*butyric acid on hydrolysis. T. H. P.

Preparation of Sulphinanilides by Means of Grignard's Reaction. A. SONN and E. SCHMIDT (*Ber*., 1924, **57**, [*B*], 1355—1356).—*Benzenesulphinanilide*, Ph·SO·NHPh, m. p. 112—113°, *phenylmethanesulphinanilide*, m. p. 144—145°, and *ethanesulphinanilide*, m. p. 72°, are prepared from thionylaniline, PhN:S:O, and the requisite Grignard reagent in ethereal solution. H. W.

Amine Oxides derived from 4-Bromodimethylaniline and from 3- or 4-Nitrodimethylaniline. L. W. JONES and E. B. HARTSHORN (*J. Amer. Chem. Soc*., 1924, **46**, 1840—1855).—The various interpretations offered to explain the isomerides of $\mathrm{NMe_3(OMe)OH}$ discovered by Meisenheimer (cf. A., 1913, i, 595, 1048), especially those of Jones and of Michael, and the more recent explanations of Lewis and Langmuir, are discussed. An attempt to prepare isomerides of the same type from oxides of substituted dimethylaniline was not successful since such amine oxides do not react with alkyl halides as methyl iodide reacts with trimethylamine oxide. Permonosulphuric acid oxidises the tertiary amines to the oxides, which crystallise from solution as neutral or acid sulphate. The corresponding hydrochlorides are stable, crystalline salts, but the hydriodides decompose, yielding free iodine and the original amine. *p*-Bromodimethylaniline oxide hydriodide was isolated below 0°. The free bases do not liberate iodine from potassium iodide, unlike the alkylpiperidine oxides (cf. Wernick and Wolffenstein, A., 1898, i, 536). Solutions of the free amine oxides were obtained by shaking the hydrochlorides in methyl alcohol with moist silver oxide. The solid bases were difficult to isolate, but were obtained in fair purity by removing the methyl alcohol rapidly under diminished pressure. Sublimation, even in a vacuum, causes decomposition, traces of formaldehyde being given off. The chief point of differentiation from the aliphatic amine oxides is in their behaviour with methyl iodide (cf. A., 1899, i, 682). No additive products with the amine oxide are formed, but the oxide is reduced and iodine liberated without the production of formaldehyde. An excess of iodine yields periodides of the quaternary salts of the amines in most cases, *e.g.*, *m*-$NO_2\cdot C_6H_4\cdot NMe_3I\cdot I_2$. The following compounds were prepared: 4-*Bromodimethylaniline oxide*, brown, very hygroscopic powder, m. p. 167—168°, probably not pure; *sulphate*,

$$C_{16}H_{22}O_6Br_2N_2S,$$

darkens above 125° and explodes at 132—135°; *hydrochloride*, darkens above 160°, decomp. 165—166°; *hydriodide*, decomp. 92—94°; *picrate*, m. p. 126—127° (decomp.). 4-*Bromophenyltrimethylammonium iodide*, decomp. 187—187·5°, *periodide*, m. p. 165—166°. 4-*Nitrodimethylaniline oxide*, m. p. 110—111°, odour like coumarin; *hydrogen sulphate*, decomp. 147—149°; *hydrochloride*, decomp. 168—169°; *picrate*, m. p. 148—159°. Reduction of the hydrogen sulphate with sulphur dioxide gave mainly 4-nitrodimethylaniline, but also small amounts of what were assumed to be 5-nitro-2-dimethylaminobenzenesulphonic acid and 2-nitro-5-dimethylaminobenzenesulphonic acid. No quaternary salt was formed with methyl iodide; a small amount of a *periodide*, m. p. 162—163°, was separated from the main reduction product. 3-*Nitrodimethylaniline oxide*, m. p. 152—155°, has a slight odour of carbylamine; *hydrochloride*, decomp. 157—158°; *picrate*, m. p. 141—142°. m-*Nitrophenyltrimethylammonium iodide*, yellow prisms, decomp. about 200°; *periodide*, bronze plates, m. p. 144—145°.

A. C.

Catalytic Alkylation of Aniline. A. B. Brown and E. E. Reid (*J. Amer. Chem. Soc.*, 1924, **46**, 1836—1839).—Using silica gel as catalyst, a quantitative study of the alkylation of aniline by methyl, ethyl, *n*-propyl, and *n*-butyl alcohols has been made. The vapours of the mixture were passed over the catalyst at various temperatures (300—500°) until that at which the maximum conversion took place was found. The percentages of alkylanilines found and the ratios of monoalkyl to dialkyl at approximately optimum temperatures are as follows: series I for $NH_2Ph : ROH =$ 1 : 1·05, and series II, 1 : 2·05. Methyl, I 37·8%, 5 : 2 at 365°; II 42%, 5 : 3 at 370°. Ethyl, I 41·5%, 5 : 1 at 385°; II 60·0%, 7 : 2 at 385°. *n*-Propyl, I 38·8%, 14 : 3 at 385°; II 54·8%, 3 : 1 at 385°. *n*-Butyl, I 32·0%, 31 : 10 at 385°; II 40·3%, 33 : 10 at 400°. The catalyst was found to have a dehydrating and also a dehydrogenating effect on the alcohols, especially at higher temperatures, gaseous hydrocarbons of the C_nH_{2n} type being evolved together with hydrogen. The activity of the catalyst fell off rapidly in the first hour and then more slowly. This falling-off was not so marked if the catalyst was not heated to a high temperature. Fouling of the catalyst is to be expected owing to the formation of condensation products from aniline and aldehydes, which easily polymerise.

A. C.

***n*-Amylaniline.** L. G. Radcliffe and R. Grindley (*J. Soc. Dyers and Col.*, 1924, **40**, 290—292).—The preparation of *n*-butylaniline, *n*-amylaniline, and *n*-diamylaniline indicates that the reaction between aniline and an alkyl halide proceeds less smoothly and with much smaller yields as the molecular weight of the alkyl halide is increased. A good yield of n-*amylaniline* was obtained by heating equimolecular proportions of aniline and *n*-amyl bromide or chloride under pressure at 190° for 6 hrs. The crude product was purified by fractional distillation, conversion into phenyl-*n*-amylnitrosoamine, and subsequent reduction by means of zinc dust and glacial acetic acid. n-*Amylaniline*, colourless oil, b. p. 260—262° (uncorr.), darkens when exposed to light. *Phenyl*-n-*amylnitrosoamine*, a greenish-yellow oil, slightly volatile in steam, decomposes when heated above 100°, and yields *p*-nitroso-*n*-amylaniline when treated with alcoholic hydrogen chloride. n-*Diamylaniline*, b. p. 280—285°, is produced by heating equimolecular proportions of *n*-amylaniline and *n*-amyl chloride under pressure at 190—200° for 2 hrs. Attempts to prepare the acetyl and benzoyl derivatives of *n*-amylaniline were unsuccessful. A. J. H.

Titanous Salts as Reducing Agents. E. KNECHT (*J. Chem. Soc.*, 1924, **125**, 1537—1546).—If an acceptor, such as a primary aromatic amine, is present in solution, and the reactants are present in the ratio $2TiCl_3 : HNO_3$, titanous chloride will reduce nitric acid to nitrous acid; a quantitative yield of the diazonium compound can be obtained in this manner. When 1-nitronaphthalene is reduced with titanous chloride in presence of a large excess of hydrochloric acid, the principal product (94%) is 4-chloro-α-naphthylamine.

[With (MISS) E. HIBBERT.]—Volumetric methods employing titanous chloride have been worked out for the determination of a number of organic compounds, including phenolphthalein, phenylhydrazine, tartrazine, tetramethyldiaminobenzhydrol, gallein, and isatin. S. B.

Oxidation of Didiphenylylamine. W. BÜLOW (*Ber.*, 1924, **57**, [*B*], 1431—1434).—Oxidation of didiphenylylamine, $NH(C_{12}H_9)_2$ (cf. Wieland and Süsser, A., 1911, i, 570), by sodium dichromate in the presence of glacial acetic acid and a little sulphuric acid, yields a dark green substance which is reduced by zinc dust to a substance, $C_{48}H_{36}N_2$, m. p. 276°, identical with the product obtained by Wieland and Süsser (*loc. cit.*) by the fission of tetradiphenylylhydrazine with ethereal hydrogen chloride; it is regarded as *o*-diphenylylaminotridiphenylylamine,

$$C_6H_3Ph(NH{\cdot}C_6H_4Ph)[N(C_6H_4Ph)_2].$$

In addition, diphenopiperazine, $C_6H_3Ph{<}\substack{N(C_6H_4Ph)\\N(C_6H_4Ph)}{>}C_6H_3Ph$, m. p. above 345°, is produced [Wieland and Süsser (*loc. cit.*) give m. p. 325—330°].

Tridiphenylylamine, m. p. 261—262°, is obtained together with the corresponding di-derivative from *p*-iododiphenyl and *p*-aminodiphenyl and copper powder (cf. Wieland and Süsser, *loc. cit.*). With antimony pentachloride, it yields a stable additive *compound*, $C_{36}H_{27}N,SbCl_5$, m. p. 130—131° (decomp.). H. W.

Steric Relations in the Acylation of Aromatic Amines and Aminophenols. L. C. RAIFORD, R. TAFT, and H. P. LANKELMA (*J. Amer. Chem. Soc.*, 1924, **46**, 2051—2057).—An examination of the acetylation of thirteen substituted anilines by Sudborough's method (T., 1901, **79**, 533) indicates that the formation of a diacetyl derivative is favoured by the presence of one negative substituent (halogen or nitro) in the ortho-position to the amino group (cf. A., 1919, i, 12), and retarded by a similar substituent in the para-position. The accelerating effect is not in accordance with the relative weights of the substituents, and in the case of ortho-para substitution the two effects counterbalance. In the acylation of aminophenols with benzoyl chloride by the Schotten-Baumann process and with *p*-nitrobenzoyl chloride in pyridine or chloroform solution (cf. Fischer, A., 1920, i, 808), the presence of halogen atoms in the ortho-positions to the hydroxyl protects the hydroxyl group to a marked extent, but does not entirely prevent the formation of the *O*-acyl-*N*-acyl compound. With the symmetrical trihalogenated phenols steric hindrance is much more pronounced with benzoyl chloride than with *p*-nitrobenzoyl chloride, but only in the case of *s*-tribromoaniline was no acyl derivative obtained under these conditions. The following compounds were obtained: o-*Chlorodiacetanilide*, m. p. 86—87°; o-*iododiacetanilide*, m. p. 64—65°; 2 : 5-*dichlorodiacetanilide*, m. p. 91—92°; 2-*chloro*-4-*benzamidophenol*, m. p. 178°; 2-*chloro*-4-*benzamidophenyl benzoate*, m. p. 206°; 2-*chloro*-4-p-*nitrobenzamidophenol*, m. p. 242°; 2-*chloro*-4-p-*nitrobenzamidophenyl* p-*nitrobenzoate*, m. p. 253°; 2 : 6-*dichloro*-4-*benzamidophenol*, m. p. 198°; 2 : 6-*dichloro*-4-*benzamidophenyl benzoate*, m. p. 177°; 2 : 6-*dichloro*-4-p-*nitrobenzamidophenol*, m. p. 265°; 2 : 6-*dichloro*-4-p-*nitrobenzamidophenyl* p-*nitrobenzoate*, m. p. 246°; 2-bromo-4-benzamidophenol, m. p. 193° (cf. Meldola and Hollely, T., 1913, **103**, 182); 2-*bromo*-4-*benzamidophenyl benzoate*, m. p. 199°; 2-*bromo*-4-p-*nitrobenzamidophenol*, yellow needles, m. p. 237°; 2-*bromo*-4-p-*nitrobenzamidophenyl* p-*nitrobenzoate*, m. p. 255°; 2 : 6-*dibromo*-4-*benzamidophenol*, m. p. 208°; 2 : 6-*dibromo*-4-*benzamidophenyl benzoate*, m. p. 172°; 2 : 6-*dibromo*-4-*p*-*nitrobenzamidophenol*, m. p. 268°; 2 : 6-*dibromo*-4-p-*nitrobenzamidophenyl* p-*nitrobenzoate*, m. p. 237°; 2 : 6-di-iodo-4-nitrophenol, m. p. 155—156° (cf. Weselsky, *Annalen*, 1874, **174**, 108; Post, *ibid.*, 1880, **205**, 91); 2 : 6-di-iodo-4-aminophenol, m. p. 169—171° (cf. Seifert, *J. pr. Chem.*, 1843, [ii], **28**, 437); 2 : 6-*di-iodo*-4-*benzamidophenol*, m. p. 222°; 2 : 6-*di-iodo*-4-*benzamidophenyl benzoate*, m. p. 210—211°; 2 : 6-*di-iodo*-4-p-*nitrobenzamidophenyl* p-*nitrobenzoate*, m. p. 277°; 2 : 4 : 6-*trichlorophenyl benzoate*, m. p. 74°; 2 : 4 : 6-*trichlorophenyl* p-*nitrobenzoate*, m. p. 105—106°; 2 : 4 : 6-*tribromophenyl benzoate*, m. p. 81°; 2 : 4 : 6-*tribromophenyl* p-*nitrobenzoate*, m. p. 153—154°; 2 : 4 : 6-*tri-iodophenyl* p-*nitrobenzoate*, m. p. 181°; *phenyl* p-*nitrobenzoate*, m. p. 129°, and 2-*nitrobenzanilide*, m. p. 212°. R. B.

Mutual Solubility. III. Mutual Solubility of Glycerol and Amino and Hydroxy Compounds. R. R. Parvatiker and B. C. McEwen.—(See ii, 659.)

Aromatic Orthoformates. J. E. Driver (*J. Amer. Chem. Soc.*, 1924, **46**, 2090—2093).—The method recently described for the preparation of triphenyl orthoformate (this vol., i, 638) can be used for the preparation of the tolyl orthoformates. The action of chloroform vapour on potassium *p*-tolyloxide at 108° gives tri-*p*-tolyl orthoformate, m. p. 112° (Auwers, A., 1907, i, 400), and traces of 1-methyl-1-dichloromethyl-$\Delta^{2:5}$-*cyclo*hexadien-4-one, m. p. 53—55°, the formation of the latter compound suggesting that an unstable dichloromethoxytoluene is the first product of the reaction. Similarly, potassium *o*-tolyloxide and boiling chloroform give *tri*-o-*tolyl orthoformate*, m. p. 96°, and potassium *m*-tolyloxide at 110—120° yields *tri*-m-*tolyl orthoformate*, m. p. 50°. The tolyl orthoformates are not hydrolysed by boiling alkalis and are only slowly oxidised by boiling neutral permanganate. R. B.

Decomposition of Ethers by Metallic Sodium. II. Relative Tenacity of Different Radicals to the Oxygen Atom. P. Schorigin (*Ber.*, 1924, **57**, [*B*], 1627—1634; cf. A., 1923, i, 207).—The decomposition of mixed ethers, particularly those of the aromatic and fatty-aromatic series, by sodium occurs in accordance with the scheme: $R{\cdot}O{\cdot}R^1+2Na \longrightarrow RR^1O{\cdots}Na_2 \longrightarrow R{\cdot}ONa+R^1Na$ or $R{\cdot}Na+R^1{\cdot}ONa$. The reaction has been applied to the determination of the relative firmness with which the radicals are attached to the oxygen atom. As is to be expected, the reaction takes place in both possible directions, but the more firmly bound of any two radicals is found to the greater extent as alkoxide or phenoxide in the products. The groups may be arranged in order of increasing tenacity to oxygen in the order: benzyl, ethyl, *iso*amyl, β-naphthyl, α-naphthyl, phenyl. The relative positions of the naphthyl groups in the series is slightly uncertain.

Phenyl α-naphthyl ether and sodium at 140° give a mixture of phenol and α-naphthol (molecular ratio, 5 : 1) and benzene and naphthalene (1 : 10) The corresponding ratios for phenyl β-naphthyl ether are 7 : 1 and 1 : 8. αβ-Dinaphthyl ether did not give a definite result by reason of the difficulty of separating α- from β-naphthol. β-Naphthyl ethyl ether yielded β-naphthol and ethyl alcohol (4 : 1) and naphthalene, ethane, and ethylene (1 : 3·3). β-Naphthyl benzyl ether gave only β-naphthol and toluene. Phenyl benzyl ether yielded only phenol and toluene with traces of benzene; it is isomerised to some extent to benzhydrol (cf. Schorigin, this vol., i, 1188). Phenetole gave almost exclusively phenol accompanied by a very little ethyl alcohol; ethane and ethylene are produced, but, apparently, no benzene. Benzyl ethyl ether gave an inseparable mixture of little benzyl alcohol and much phenylethylcarbinol, toluene, and ethylene. Diethyl ether is decomposed by sodium at 200—340° into ethylene, probably ethane and hydrogen, and a little ethyl alcohol. Di*iso*amyl ether is decomposed with greater difficulty than the diethyl compound, yielding β-methyl-Δ^{α}-butylene, β-methyl-Δ^{β}-butylene, and *iso*pentane. H. W.

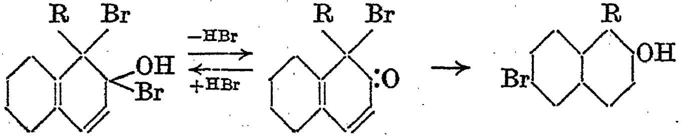
Superheating of Uniform Organic Compounds. I. Arylparaffins and Aliphatic Esters. S. Skraup and F. Nieten (*Ber.*, 1924, **57**, [*B*], 1294—1310).—The pyrogenic decomposition of anisylparaffins in sealed tubes at as low a temperature as possible leads, in the case of compounds with an even number of carbon atoms in the aliphatic chain, to the loss of the terminal methyl group (as ethylene) and production of the next lower homologue with an odd number of carbon atoms. Under similar conditions, the compounds with an odd number of carbon atoms remain unchanged, but at a slightly higher temperature they lose the complete aliphatic chain, probably as olefine, and yield anisole. The phenyl esters of stearic and palmitic acids decompose at 300—320° in sealed tubes filled with nitrogen into pentadecane and tridecane, respectively, and phenyl acrylate; the latter is converted primarily into acetylene and phenyl formate, which then yields phenol and carbon monoxide. In an open vessel, on the other hand, phenyl stearate is decomposed at 320° into carbon monoxide, possibly hydrogen and phenol; acetylene, ethylene, or paraffin hydrocarbons are not produced, the chief product being a carbonised residue.

p-*Anisyl* n-*propyl ketone*, b. p. 162—163°/20 mm., m. p. —3° to —4° (*phenylhydrazone*, m. p. 77°), is prepared by the action of aluminium chloride on a solution of anisole and butyryl chloride in light petroleum or by the action of butyryl chloride on *p*-anisylchloromercurate at 135°. If light petroleum is replaced by carbon disulphide, the yield of the ketone is decreased and the product contaminated with *αα-di*-p-*anisyl*-Δ^{α}-*butylene*, $CHEt:C(C_6H_4\cdot OMe)_2$, m. p. 95—96°. The ketone is reduced by amalgamated zinc and hydrochloric acid to *p*-butylanisole (*sulphonamide*, m. p. 96°). p-*Anisyl* n-*butyl ketone*, b. p. 165—167°/14 mm., m. p. 26° (*phenylhydrazone*, m. p. 73°), is converted similarly into p-n-*amylanisole*, b. p. 124—125°/14 mm. (*sulphonamide*, m. p. 101°). p-*Anisyl* n-*amyl ketone*, m. p. 41° (*phenylhydrazone*, m. p. 28°), p-*hexylanisole*, b. p. 152—153°/15 mm., and its *sulphonic acid*, m. p. 75°, and *sulphonamide*, m. p. 87°, are described. p-*Anisyl* n-*hexyl ketone*, b. p. 192°/17 mm., m. p. 40° (*phenylhydrazone*, m. p. 35°), gives p-*heptylanisole*, b. p. 160—162°/17 mm. (*sulphonamide*, m. p. 108°). p-*Anisyl* n-*octyl ketone*, m. p. 43° (*phenylhydrazone*, m. p. 48°), yields p-*nonylanisole*, b. p. 178—180°/18 mm.

Phenyl β-chloropropionate, b. p. 141—143°/18 mm., is converted by boiling pyridine into *phenyl acrylate*, b. p. 202—203° (slight decomp.), 105°/20 mm., and, apparently, the quaternary *compound*, $C_5H_5NCl\cdot CH_2\cdot CH_2\cdot CO_2Et$, which, however, is not an intermediate product in the formation of the acrylate.

The action of propionyl chloride on dimethylaniline in the presence of zinc chloride gives a mixture of *αα-bisdimethylaminophenyl*-Δ^{α}-*propylene* (the constitution of which is established by its oxidation to Michler's ketone) and p-*dimethylaminopropiophenone*, b. p. 270—272° (phenylhydrazone, m. p. 58°); the ketone is also prepared from propionyl chloride and dimethylaminophenylchloromercurate. Similarly, dimethylaniline, butyryl chloride, and zinc chloride yield p-*dimethylaminophenyl* n-*propyl ketone*, b. p. 180—185°/27 mm. (*phenylhydrazone*, m. p. 67—68°; *methiodide*, m. p. 163°), which does not appear to undergo reduction by Clemmensen's method, and *αα-bisdimethylaminophenyl-*Δ^{α}*-butylene*, m. p. 80—81°, which is oxidised to Michler's ketone. H. W.

Reaction Processes Underlying Substitution. K. Fries and H. Engel (*Annalen*, 1924, **439**, 232—245).—By the bromination of derivatives of β-naphthol, under definite conditions, the intermediate products are ketobromides, derivatives of 1 : 2-dihydronaphthalene. The bromination is carried out in the cold in acetic acid in presence of sodium acetate; otherwise the products are insoluble resins. By the further action of hydrogen bromide or chloride in acetic acid, the product isomerises, giving the corresponding 6-bromo-β-naphthol, the rate of isomerisation depending on the concentration of the halogen acid; the change takes place more rapidly with hydrogen bromide than with hydrogen chloride, and in the latter case no 6-chloro-β-naphthol is formed. The first step in the bromination is supposed to consist in the addition of two atoms of bromine to the 1 : 2-double bond I followed by loss of hydrogen bromide to give the bromoketone II, which in its turn is more or less easily isomerised to III. [R=Br, Me, Et.]



(I.) (II.) (III.)

1-Bromo-β-naphthol on bromination under the above conditions yields 1 : 1-*dibromo*-2-*keto*-1 : 2-*dihydronaphthalene*, m. p. 70°, unstable in light or on warming. Reduction with zinc and acetic acid regenerates the bromonaphthol, and by treatment with hydrogen bromide or chloride in acetic acid, 1 : 6-dibromo-β-naphthol is produced. By further bromination of the ketobromide, 1 : 1 : 6-*tribromo*-2-*keto*-1 : 2-*dihydronaphthalene*, m. p. 115°, is produced, which on reduction yields 1 : 6-dibromo-β-naphthol. The tribromo-compound is stable to hydrogen bromide in acetic acid at the ordinary temperature.

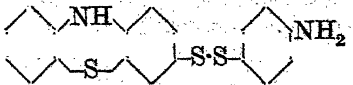
1-*Bromo*-2-*keto*-1-*methyl*-1 : 2-*dihydronaphthalene*, m. p. 80°, which is stable to dilute alkali, on reduction yields 1-methyl-β-naphthol. With silver acetate in acetic acid, the ketobromide yields 1-*acetoxy*-2-*keto*-1-*methyl*-1 : 2-*dihydronaphthalene*, and by the action of halogen acids as above, it isomerises to 6-bromo-1-methyl-β-naphthol, which forms a molecular compound with its acetyl derivative, $C_{11}H_9OBr{\cdot}C_{13}H_{11}O_2Br$, m. p. 119°. 6-*Bromo*-1-*methyl*-β-*naphthol* on bromination yields 1 : 6-*dibromo*-2-*keto*-1-*methyl*-1 : 2-*dihydronaphthalene*, yellow prisms.

1-*Ethyl*-β-*naphthol*, m. p. 105°, was obtained from 1-acetyl-β-naphthol by Clemmensen's reduction method. It is unstable in the air. The *acetyl* derivative melts at 53°. On bromination in acetic acid in the absence of sodium acetate, 6-*bromo*-1-*ethyl*-β-*naphthol* is formed, m. p. 109°; *acetyl* derivative, m. p. 138°. By bromination in presence of sodium acetate, the product is 1-*bromo*-2-*keto*-1-*ethyl*-1 : 2-*dihydronaphthalene*, m. p. 71°. By the action of hydrogen bromide in acetic acid solution, a mixture of 6-*bromo*-1-*ethyl*-β-*naphthol* and its *acetyl* derivative is formed, the proportions depending on the concentration of the halogen acid. 1 : 6-*Dibromo*-2-*keto*-1-*ethyl*-1 : 2-*dihydronaphthalene*, m. p. 103°, on reduction gives 6-bromo-1-ethyl-β-naphthol. By the action of sodium nitrite and acetic acid on the ethereal solution of the last-named compound, 6-*bromo*-1-*nitro*-2-*keto*-1-*ethyl*-1 : 2-*dihydronaphthalene* is obtained, m. p. 112°, unstable on warming. A. E. C.

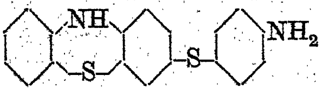
Action of Oxalyl Chloride on Naphthols. M. Giua and V. de Franciscis.—(See i, 1092.)

Ultra-violet Absorption Spectra of some Derivatives of Naphthols. S. Komatsu, B. Masumoto, and S. Kumamoto.—(See ii, 642.)

Direct Sulphuration of Aniline. H. H. Hodgson (*J. Chem. Soc.*, 1924, **125**, 1855—1858).—The initial product of the action of sulphur on aniline at 170—180° is 2 : 2′-diaminodiphenyl disulphide, but increasing quantities of 4 : 4′-diaminodiphenyl disulphide are formed with rising temperature. On prolonged heating and with excess of aniline, the disulphides undergo transformation into 2 : 2′-diaminodiphenyl sulphide, 2 : 4′-diaminodiphenyl sulphide, and 4 : 4′-diaminodiphenyl sulphide. On heating with excess of sulphur, by diphenylamine condensation and further sulphuration a *substance*, $C_{18}H_{14}N_2S_3$, is produced to which the structure (I) is assigned, together with its desulphuration product,



(I.)



(II.)

$C_{18}H_{14}N_2S_2$ (II). The latter yields a brilliant red pigment when diazotised and coupled with β-naphthol. The azo-β-naphthol derivative of 4 : 4′-diaminodiphenyl disulphide is described. Merz and Weith's thioaniline from sulphur and boiling aniline (*Ber.*, 1871, 4, 384) is 2 : 4′-diaminodiphenyl sulphide with a little 4 : 4′-diaminodiphenyl sulphide; their product in the presence of lead oxide is the latter sulphide (cf. Nietzki and Bothof, A., 1895, i, 132). Lead oxide thus promotes para-substitution (cf. Hodgson and Dix, T., 1914, **105**, 952). R. B.

Mechanism of Aniline Thionation [Sulphuration] with Observations on the Therapeutical Importance of the Dithioanilines. H. H. Hodgson (*J. Soc. Dyers and Col.*, 1924, **40**, 330—337).—A restatement of results already reported (preceding abstract). W. A. S.

Transformation of Benzyl Ethers into Carbinols. I. P. Schorigin (*Ber.*, 1924, **57**, [*B*], 1634—1637).—The action of sodium on phenyl benzyl ether at 100° (cf. Schorigin, i, 1185), leads to the production of benzhydrol in 30—35% yield. Benzyl ethyl ether and β-naphthyl benzyl ether similarly give phenylethylcarbinol and phenyl-β-naphthylcarbinol. The presence of the benzyl group in the ether appears to be essential for the transformation, $CH_2Ph·O·R \rightarrow CHPh(OH)·R$. H. W.

Preparation of Alcohols from Aldehydes. BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 384351; from *Chem. Zentr.*, 1924, i, 2398).—Alcohols are prepared from aldehydes by reduction with hydrogen in the presence of activated magnesium. Examples are given of the preparation of cinnamyl alcohol, geraniol, b. p. 114—116°/13 mm., citronellol, b. p. 117—119°/17 mm., β-phenylpropyl alcohol, b. p. 104—106°/10 mm., heptyl alcohol, b. p. 78—80°/12·5 mm., phenylethyl alcohol, and benzyl alcohol from the corresponding aldehydes. G. W. R.

Intramolecular Change. Identification of the Products of Dehydration of ααγ-Triphenyl-ββ-dimethylpropan-α-ol. (MME.) P. RAMART (*Compt. rend.*, 1924, **179**, 400—402).—Magnesium benzyl chloride condenses readily with αα-diphenylethyl methyl ketone (ββ-diphenylbutan-γ-one) giving *ααγ-triphenyl-β-methylbutan-β-ol*, $CPh_2Me·C(OH)Me·CH_2Ph$, m. p. 78—80°, b. p. 225—230°/3 mm., which on dehydration with a mixture of acetyl chloride and acetic anhydride, or by warming with infusorial earth, yields a mixture of two hydrocarbons, m. p. 110° and 90° respectively, which are identical with those previously obtained by the dehydration of ααγ-triphenyl-ββ-dimethylpropan-α-ol (this vol., i, 1062). The two hydrocarbons are regarded as stereoisomeric forms of ααγ-triphenyl-β-methyl-Δ^{γ}-butene, $CPh_2Me·CMe{:}CHPh$. Their formation from ααγ-triphenyl-ββ-dimethylpropan-α-ol involves an intramolecular change prior to dehydration:

$$CPh_2(OH)·CMe_2·CH_2Ph \longrightarrow CPh_2Me·C(OH)Me·CH_2Ph.$$

The possibility of the alternative change

$$CPh_2(OH)·CMe_2·CH_2Ph \longrightarrow CH_2Ph·CPh_2·CMe_2·OH$$

is excluded, since the *γγδ-triphenyl-β-methylbutan-β-ol*, b. p. 205—210°/1 mm., obtained in 80—100% of the theoretical yield from magnesium methyl iodide and benzyl diphenylbenzylacetate, is dehydrated with difficulty, even by phosphoric anhydride, yielding a mixture of unchanged alcohol and a *hydrocarbon*, $C_{23}H_{22}$, b. p. 196—199°/3 mm., 235—236°/25 mm., which does not take up bromine. R. B.

Transformation of Cinnamaldehyde into Cinnamyl Alcohol, and the Constitution of Cubebin. H. PAULY, H. SCHMIDT, and E. BÖHME (*Ber.*, 1924, **57**, [*B*], 1327—1330).—The reduction of cinnamaldehyde diacetate by iron and acetic acid (Barbier and Léser, A., 1905, i, 653) depends essentially on the action of ferrous acetate on cinnamaldehyde whereby cinnamyl alcohol (diphenylurethane, m. p. 98°; *phenylurethane*, m. p. 91—91·5°) is produced. γ-Hydroxy-αζ-diphenylhexane, b. p. 130—136°/2 mm. (cf. von Braun and Kochendörfer, A., 1923, i, 1197), is formed as by-product together with resinous material. Piperonylacraldehyde is reduced in a similar manner to *β-piperonylallyl alcohol*, m. p. 123°. This substance is not identical with cubebin, to which its structure has been assigned (cf. Mameli, A., 1922, i, 347). Cinnamaldehyde cannot be converted into cinnamyl alcohol and cinnamic acid by Cannizzaro's reaction to an extent greater than 10%. H. W.

Benzeins. III. R. MEYER and E. FUNKE (*Ber.*, 1924, **57**, [*B*], 1360—1363).—Schroeter's "dihydroxydimethyltriphenylcarbinol," prepared by the action of benzotrichloride on *o*-cresol, loses a molecular proportion of water when heated at 140—150°, and is therefore to be regarded as *o*-cresolbenzein,

$$C_6H_3Me(OH)\cdot CPh{:}C_6H_3Me{:}O,H_2O.$$

It is conveniently purified through the *hydrochloride*. The *dibenzoate*, m. p. 134°, is described. Addition of hydrogen cyanide to *o*-cresolbenzein yields the colourless *cyanohydrin*,

$$CN\cdot CPh[C_6H_3Me(OH)]_2,$$

m. p. 147°, which is converted by benzoyl chloride in the presence of sodium hydroxide into *dibenzoxydimethyltriphenylmethanecarboxylamide*, $NH_2\cdot CO\cdot CPh(C_6H_3Me\cdot OBz)_2$, m. p. 56°. *o*-Cresolbenzein is transformed by an excess of bromine in glacial acetic acid solution into *dibromo-o-cresolbenzein*, $C_6H_2BrMe(OH)\cdot CPh{:}C_6H_2BrMe{:}O,H_2O$, which loses a molecular proportion of water at 140°; it yields a blue *sodium* salt, $C_{21}H_{15}O_2Br_2Na,H_2O$.

Dihydroxydimethyltriphenylmethane, m. p. 170°, is prepared by the condensation of benzaldehyde with *o*-cresol in the presence of sulphuric acid. H. W.

Sulphonefluorescein and Dihydroxybenzoylbenzene-*o*-sulphonic Acid, and some of their Derivatives. W. R. ORNDORFF and R. S. VOSE (*J. Amer. Chem. Soc.*, 1924, **46**, 1896—1912).—Sulphonefluorescein has only been obtained previously in the amorphous condition and of doubtful purity. Five different methods of preparation are described. Heating resorcinol with "saccharin" and sulphuric acid at 135—140° gives a 52% yield, whilst *o*-sulphobenzoyl chloride with resorcinol at 100° gives 41% of the theoretical yield. Contrary to Fahlberg and Barge and to White (A., 1896, i, 49; 1889, 709), it is obtained on heating *o*-sulphobenzoic anhydride with resorcinol at 135—140°, the reaction taking place in two stages with formation of *o*-2 : 4-dihydroxybenzoylbenzenesulphonic acid as intermediate product. Sulphonefluorescein separates in red needles with a blue surface colour which causes them to appear purple. When finely divided (rapid precipitation or grinding) it is bright yellow. Similarly prepared alkaline solutions of sulphonefluorescein and ordinary fluorescein are indistinguishable by the unaided eye, although the fluorescence of sulphonefluorescein is 10% more intense than that of fluorescein. In both cases the fluorescence spectrum consists of a single band extending approximately from λ 5000 to λ 5900, with a maximum at λ 5249 for sulphonefluorescein and at λ 5209 for fluorescein. Sulphonefluorescein gives rise to coloured quinonoid and colourless lactoid derivatives. Sulphonefluorescein itself does not occur in the lactoid form, but is probably a solid solution of the quinonoid form (as an oxonium or carbonium salt) and the quinonoid hydrate. It acts as a monobasic acid and forms highly coloured salts, soluble in water with a green fluorescence: the *ammonium* salt is a dark red powder containing $2H_2O$; *barium* salt, and *zinc* salt ($7H_2O$), orange crystals. On reduction with zinc dust in water sulphonefluorescein is converted into the *zinc* salt of *sulphonefluorescin*, a nearly colourless solid which becomes yellow in air and on heating in air at 120—125° is changed to the orange-red salt of the fluorescein. *Sulphonefluorescin* forms straw-coloured crystals when isolated from the zinc salt. It is extremely soluble in water (in contrast to the unreduced substance). The solution in sodium hydroxide is colourless and almost non-fluorescent, but marked fluorescence appears on standing. *Sulphonefluorescin diacetate* has m. p. 230° (decomp.). Exposed to dry ammonia, sulphonefluorescein takes up 4 mols., 3 of which are lost on exposure to concentrated sulphuric acid. A *dianilino* compound, green crystals which do not melt at 320°, probably an inner ammonium salt, is formed on boiling sulphonefluorescein with aniline. *Sulphonefluorescein monoacetate*, dark green crystals, decomp. without melting above 300°, and the *monobenzoate*, yellow crystals, which dissolve in sodium hydroxide to deep purple solution, have the quinonoid structure; the *diacetate*, orange-yellow crystals, decomp. 209°, has the lactoid structure. Sulphonefluorescein reacts both with benzoyl chloride and phosphorus pentachloride to form the same *dichloride*, colourless, decomp. 320°, in which the chlorine atoms have replaced the hydroxyl groups. This forms a disodium (coloured) and a trisodium salt (colourless), and a *hydrate*, $C_{19}H_{10}O_4Cl_2S,H_2O$, red, orange to greenish-orange by transmitted light. *Dibromosulphonefluorescein*, red needles with silky lustre, not melting at 300°, is soluble in dilute alkali forming solutions intensely green by reflected light and orange to red by transmitted light. The tetrabromo compound described by Sisley could not be made. The *diacetate*, which does not melt at 300°, is hydrolysed by water. It absorbs 4 mols. of ammonia and loses 3 of them over concentrated sulphuric acid. *Di-iodosulphonefluorescein*, red needles, forms a *diacetate*, short, yellow prisms, dark red at 315°. *o*-2 : 4-Dihydroxybenzoylbenzenesulphonic acid, prepared from the ammonium salt (containing $3H_2O$), behaves as a monobasic acid towards methyl-red, but as dibasic to phenolphthalein. The 3 : 5-*dibromo* derivative, m. p. 110—112°, contains $2{\cdot}5H_2O$. It titrates as a dibasic acid with both of the above indicators. A. C.

Simple Synthesis of the Salts of N-Benzylideneamino-acids. O. GERNGROSS and E. ZÜHLKE (*Ber.*, 1924, **57**, [*B*], 1482—1489).—The sodium salts of arylideneamino-acids are obtained in almost quantitative yield by the action of an alcoholic solution of sodium ethoxide on an alcoholic solution of the ester of the amino-acid and the requisite aldehyde. Hydrolysis is ascribed to the action of sodium hydroxide formed from the ethoxide and water liberated by the partial condensation of the aldehyde and ester. The separation of the sodium salt disturbs the equilibrium established otherwise between amino ester, aldehyde, and arylideneamino ester and thus causes the completion of the reaction. The arylidene derivatives are very stable towards alkali hydroxide, but are hydrolysed with great ease by acids.

Ethyl p-*nitrobenzylideneaminoacetate*, $NO_2\cdot C_6H_4\cdot CH:N\cdot CH_2\cdot CO_2Et$, m. p. 148°, is readily prepared from ethyl aminoacetate and benzaldehyde in alcoholic solution. *Methyl* l-α-p-*nitrobenzylideneamino*-β-*hydroxyphenylpropionate*, m. p. 125°, is obtained similarly.

Sodium benzylideneaminoacetate, decomp. 255—260°, results from the action of sodium ethoxide on ethyl aminoacetate and benzaldehyde in alcoholic solution; the *copper*, *calcium*, and *silver* salts are described. *Sodium* α-*benzylideneaminopropionate*, *sodium* l-α-*benzylideneamino*-β-*hydroxyphenylpropionate*, decomp. 275° after darkening at 240°, and the hygroscopic sodium salt of benzylideneglycylglycine are similarly prepared.

[With J. ROTHE.]—*Sodium piperonylideneaminoacetate*, m. p. 232°, is prepared from glycine ester hydrochloride, sodium ethoxide, and piperonal.

[With J. JODÉ.]—Contrary to the observations of Puxeddu (A., 1909, i, 720), 5-*o*-nitrobenzylideneaminosalicylic acid is rather more resistant than the corresponding derivatives of aliphatic acids towards hydrochloric acid, but is smoothly hydrolysed by the mineral acid at varying concentrations into its components without giving indications of the formation of a hydrochloride. H. W.

Action of Triphenylmethyl Chloride on Ethyl β-Aminocrotonate and Analogous Compounds. E. BENARY and P. LORTH (*Ber.*, 1924, **57**, [*B*], 1324—1327).—Triphenylmethyl chloride resembles acyl chlorides (A., 1923, i, 37, and previous abstracts) in its ability to react with β-aminocrotonic esters and related substances. It appears generally to yield only *N*-derivatives and to react only with compounds containing the unsubstituted amino group.

Ethyl β-aminocrotonate is converted by triphenylmethyl chloride in the presence of pyridine at 100° into *ethyl* β-*triphenylmethylaminocrotonate*, $CH_3\cdot C(NH\cdot CPh_3):CH\cdot CO_2Et$, m. p. 137—138°, which is inactive towards phenylhydrazine and is converted by alcoholic potassium hydroxide solution into *acetonetriphenylmethylimide*, $CMe_2:N\cdot CPh_3$, m. p. 162° (*tribromide*, m. p. 235° after darkening at 230°). β-*Triphenylmethylaminocrotonanilide*, m. p. 209°, β-*triphenylmethylaminocrotononitrile*, m. p. 250—251°, N-*triphenylmethylbenzoacetodinitrile*, $CPh_3\cdot NH\cdot CPh:CH\cdot CN$, m. p. 228—229°, N-*triphenylmethylacetylacetoneamine*, $CHAc:CMe\cdot NH\cdot CPh_3$, m. p. 161°, and N-*triphenylmethylbenzoylacetoneamine*,

$$CHBz:CMe\cdot NH\cdot CPh_3,$$

m. p. 192—193°, are prepared similarly. H. W.

Preparation of Anilides and Esters. E. DE B. BARNETT and I. G. NIXON (*Chem. News*, 1924, **129**, 190—191).—Excellent yields of anilides and esters are obtained by slowly adding thionyl chloride (1 mol.) to a well-cooled equimolecular solution of the acid and phenol or primary amine in pyridine, the mixture being poured into water after 1 hour at the ordinary temperature. Phenylacetic acid gives very poor results, and the method fails with diphenylamine and 1-aminoanthraquinone; with aliphatic alcohols, the results are uncertain. The following corrected m. p. are given: *iso*eugenyl benzoate, 106°; β-naphthyl *p*-nitrobenzoate, 169°; *o*-nitrophenyl *m*-nitrobenzoate, 129°; *m*-tolyl *p*-nitrobenzoate, 90°; *p*-nitrobenzanilide, 216°; *p*-nitrobenzo-*p*-nitroanilide, 274°; *p*-nitrobenzo-*o*-nitroanilide, 277°. The following compounds are new: o-*nitrophenyl* o-*nitrobenzoate*, m. p. 125°; o-*nitrophenyl anisate*, m. p. 96°; p-*nitrophenyl* o-*nitrobenzoate*, m. p. 111°; p-*nitrophenyl* p-*nitrobenzoate*, m. p. 159°; p-*nitrophenyl anisate*, m. p. 166°; p-*nitrophenyl* 3 : 5-*dinitrobenzoate* (+1 mol. acetic acid), m. p. 188°; *pyrocatechyl di*-p-*nitrobenzoate*, m. p. 169°; *quinyl di*-p-*nitrobenzoate*, m. p. 258°; β-*naphthyl* o-*nitrobenzoate*, m. p. 112°; β-*naphthyl* m-*nitrobenzoate*, m. p. 134°. R. B.

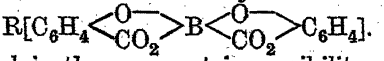
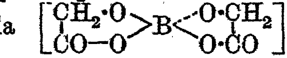
Pressor Anæsthetics. I. C. S. MARVEL and V. DU VIGNEAUD (*J. Amer. Chem. Soc.*, 1924, **46**, 2093—2099).—Three compounds have been prepared which contain both the grouping Ph·C·C·N< characteristic of pressor activity (Barger and Dale, A., 1910, ii, 984) and $Ph\cdot CO\cdot O\cdot C\cdot C\cdot NR_2$, characteristic of local anæsthetic power (Pyman, T., 1908, **93**, 1796; 1917, **111**, 1121). Two of the compounds, 2-diethylamino-1-hydrindyl *p*-aminobenzoate hydrochloride and 2-di-*n*-butylamino-1-hydrindyl *p*-aminobenzoate hydrochloride, have only a very slight anæsthetic action, that of the diethylamino compound being the greater, whilst the third compound, α-phenyl-β-diethylaminoethyl *p*-aminobenzoate hydrochloride (phenylprocaine), has a strong anæsthetic action and a low toxicity. None of these three compounds showed any appreciable pressor action, and there is no record of the pressor activity of a similar compound containing both linkings, $CH_2O_2\cdot C_6H_3\cdot CH(CO_2Ph)\cdot CH_2\cdot NMe_2$ (Pyman, T., 1908, **93**, 1796), or of the benzoyl esters of ethyl- and diethyl-mydriatine.

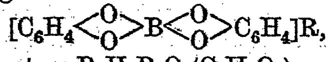
2-Bromo-1-hydroxyhydrindene (Pope and Read, T., 1912, **101**, 762) readily condenses with *p*-nitrobenzoyl chloride in benzene solution in the presence of pyridine, giving 2-*bromo*-1-*hydrindyl* p-*nitrobenzoate*, m. p. 131°, which could not be condensed with diethylamine. Diethylamine and 2-bromo-1-hydroxyhydrindene readily give 2-*diethylamino*-1-*hydroxyhydrindene*, b. p. 165—167°/15 mm., d^{20} 1·043, n_D^{20} 1·5393, which readily turns red in the air, in 56—60% yield (*hydrochloride*, m. p. 175°); it condenses with *p*-nitrobenzoyl chloride in the presence of pyridine giving (yield 50—59%) 2-*diethylamino*-1-*hydrindyl* p-*nitrobenzoate*, yellow crystals, m. p. 85°. The *hydrochloride*, m. p. 210—212°, is obtained by condensing in the absence of pyridine, and on reduction with iron yields 2-*diethylamino*-1-*hydrindyl* p-*aminobenzoate hydrochloride*, m. p. 206° (yield 48%). Similarly, di-*n*-butylamine and 2-bromo-1-hydroxyhydrindene in benzene solution give in 63—65% yield, 2-*di*-n-*butylamino*-1-*hydroxyhydrindene*, rapidly turning red, b. p. 155—165°/7 mm., n_D^{29} 1·493, which with *p*-nitrobenzoyl chloride in benzene solution gives, in 60—67% yield, 2-*di*-n-*butylamino*-1-*hydrindyl* p-*nitrobenzoate hydrochloride*, m. p. 155—156°. Reduction of the hydrochloride with iron in neutral solution gives, in 72—

85% yield, *2-di-*n*-butylamino-1-hydrindyl* p*-aminobenzoate*, m. p. 74° (*hydrochloride*, m. p. 229—230°, *hydrogen sulphate*, m. p. 200—201°). ω-Chloroacetophenone and diethylamine in benzene solution yield *ω-diethylaminoacetophenone*, b. p. 148—152°, n_D^{23} 1·5180, which on reduction by Adams and Voorhees' method (A., 1922, ii, 558) yields *α-phenyl-β-diethylaminoethyl alcohol*, n_D^{26} 1·507, and this with *p*-nitrobenzoyl chloride in benzene solution gives (yield 89—91%) *α-phenyl-β-diethylaminoethyl* p*-nitrobenzoate hydrochloride*, m. p. 155—156° (*nitrate*, m. p. 161·5°, insoluble in water) from which by reduction with iron at 45—50° is obtained *α-phenyl-β-diethylaminoethyl* p*-aminobenzoate*, m. p. 88—89° (*hydrochloride*, m. p. 210—212°). R. B.

Preparation of Acid Anhydrides. E. de B. Barnett and J. W. Cook (*Chem. News*, 1924, **129**, 191).—Acid anhydrides may be obtained in about 70% of the theoretical yield by treating the acid (2 mols.), in ice-cold pyridine, with thionyl chloride (1 mol.) and keeping the mixture at the ordinary temperature for 3 hrs. The anhydrides are isolated either by pouring into cold dilute hydrochloric acid, or by fractional distillation of the reaction mixture. Almost quantitative yields are obtained with *p*-toluic acid and anisic acid, but the method fails with palmitic, stearic, phenylacetic, *o*- and *p*-nitrobenzoic, and 3 : 5-dinitrobenzoic acids. R. B.

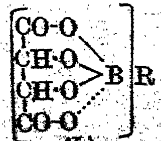
Internally Complex Borates. A. Rosenheim and H. Vermehren (*Ber.*, 1924, **57**, [*B*], 1337—1342).—The constitution of a series of borates is most simply explained by regarding them as complex salts of tervalent boron in which the element, as in the anion BF_4', has the co-ordination number 4.

Analysis of the *sodium*, *potassium*, *lithium*, *calcium* (+$6H_2O$), and *copper* salts of Jahn's "borodisalicylic acid" are in agreement with the structure  $R[C_6H_4{<}\genfrac{}{}{0pt}{}{O—}{CO_2}{>}B{<}\genfrac{}{}{0pt}{}{O—}{CO_2}{>}C_6H_4]$. Jahn's formulation does not explain the apparent impossibility of forming salts containing two equivalents of alkali. *o*-Hydroxytoluic acid forms well-crystallised compounds with borates of which the *calcium* salt, $C_{32}H_{24}O_{12}B_2Ca,5H_2O$, is described. Glycollic acid yields salts of the formula  $\left[\begin{array}{l}CH_2\cdot O\\ |\\ CO-O\end{array}{>}B{<}\begin{array}{l}O\cdot CH_2\\ \quad\ \ |\\ O\cdot CO\end{array}\right]R$, of which the *potassium*, *ammonium*, *sodium*, and *calcium* compounds are described. Analyses of the pyrocatechol–boric acid derivatives (sodium, potassium, and ammonium salts) agree with the formula



$$[C_6H_4{<}\genfrac{}{}{0pt}{}{O}{O}{>}B{<}\genfrac{}{}{0pt}{}{O}{O}{>}C_6H_4]R,$$

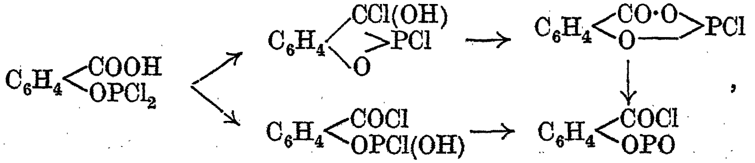
but not with the structure $R_2H_2B_2O_4(C_6H_4O_2)_3$, assigned by Böeseken (A., 1918, i, 219). Similarly, the tartaric acid borates are considered to be internally complex salts (I) rather than boryl derivatives,



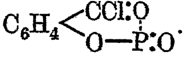
(I.)

$CO_2R\cdot CH(OH)\cdot CH(OH)\cdot CO_2\cdot BO$; like considerations are extended to the antimonyl compounds. H. W.

Reaction between the Chlorides of Phosphorus and *o*-, *m*-, and *p*-Hydroxybenzoic Acids. L. Anschütz (*Annalen*, 1924, **439**, 265—275).—The constitution of the product of the interaction of phosphorus trichloride and salicylic acid (R. Anschütz and Emery, A., 1887, 947; 1890, 53) is *o-phosphitobenzoyl chloride*, $O{:}PO{\cdot}C_6H_4{\cdot}COCl$. With *p*-toluidine in absolute ether, followed by hydrolysis with hot water, salicyloyl-*p*-toluidide is formed. Traces of phosphine, phosphorous and phosphoric acids were also detected. To test the suggestion that the reaction between phosphorus pentachloride and salicylic acid (cf. R. Anschütz, A., 1906, i, 502) proceeds in two stages, the second being the interaction of phosphorus oxychloride and salicyloyl chloride, the two latter were heated together in equimolar proportions, but no evidence of combination was forthcoming. The alternate suggestion, that with either the trichloride or the pentachloride of phosphorus the phenolic hydroxyl group of the salicylic acid is first attacked, is supported by the ready interaction of phenol and phosphorus trichloride. The following scheme is put forward:


$C_6H_4<{COOH \atop OPCl_2}$
C_6H_4 CCl(OH) >PCl O
$C_6H_4<{CO{\cdot}O \atop O}>PCl$
$C_6H_4<{COCl \atop OPCl(OH)}$
$C_6H_4<{COCl \atop OPO}$

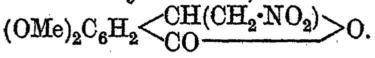
with the corresponding scheme for the interaction between the acid and phosphorus pentachloride.

By heating *m*- or *p*-hydroxybenzoic acid (1 mol.) with phosphorus trichloride (2 mols.) at 120°, no *m*- or *p*-phosphitobenzoyl chloride was obtained. The *o*-phosphitobenzoyl chloride exists in a comparatively stable state, probably owing to a saturation of the partial valency,  $C_6H_4<{CCl{:}O \atop O{-}P{:}O}$. Unsuccessful attempts were made to synthesise phosphitobenzene, PhOPO, from phenoxyphosphorus dichloride and anhydrous oxalic acid at 80—90°, and by the action of benzoic acid on the dichloride at 90°, whereby benzoyl chloride and phenyl benzoate were isolated on subsequent distillation under diminished pressure. A. E. C.

Reduction Product of *o*-Nitromandelonitrile. G. Heller (*Ber.*, 1924, **57**, [*B*], 1501—1502).—In reply to Reissert and Hessert (this vol., i, 853), the author slightly modifies his original conception (A., 1906, i, 585), but considers the reduction-product of *o*-nitromandelonitrile to be a double hydrochloride of hydroxylaminomandelamide and dihydroxylaminomandelonitrile instead of hydroxylaminomandelamide hydrochloride as proposed by these authors. H. W.

[**Benzilic Acid Transformation.**] A. Schönberg (*Ber.*, 1924, **57**, [*B*], 1396—1397; cf. Schönberg and Keller, A., 1923, i, 928).—A reply to the criticisms of Lachman (this vol., i, 653). H. W.

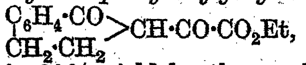
Nitromethylmeconine. W. Rodionow and S. Kagan (*Ber.*, 1924, 57, [*B*], 1442—1443).—With the object of preparing 5 : 6-dimethoxy-2-ω-nitrovinylbenzoic acid, opianic acid has been condensed with nitromethane. The product, m. p. 166—167°, is, however, stable towards bromine or permanganate, and insoluble in cold but soluble in hot sodium carbonate solution. It is therefore regarded as *ω-nitromethylmeconine*,



$$(OMe)_2C_6H_2<\begin{matrix}CH(CH_2\cdot NO_2)\\ CO\end{matrix}>O.$$

H. W.

Preparation of γ-*o*-Carboxyphenyl-*n*-butyric Acid. W. Hückel and E. Goth (*Ber.*, 1924, 57, [*B*], 1285—1290).—*Ethyl 1-keto-1 : 2 : 3 : 4-tetrahydronaphthyl-2-glyoxylate*,

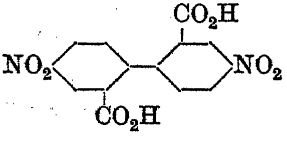


$$\begin{matrix}C_6H_4\cdot CO\\ |\quad\quad\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CO\cdot CO_2Et,$$

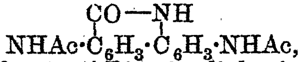
m. p. 48°, prepared in 90% yield by the condensation of 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene with ethyl oxalate in the presence of ethyl-alcoholic sodium ethoxide, loses carbon monoxide when heated and yields *ethyl* 1-*hydroxy*-3 : 4-*dihydronaphthalene*-2-*carboxylate*, m. p. 34° (the corresponding *copper* salt, m. p. 196°, and the free *acid*, m. p. 93° [decomp.] are described). The ester does not readily undergo fission under the influence of alkali but is transformed by a solution of sodium in boiling *cyclo*hexanol into γ-*o*-carboxyphenyl-*n*-butyric acid, m. p. 139—140°, in 20% yield; 3 : 4-*dihydronaphthalene-2-carboxylic acid*, m. p. 120°, tetrahydro-β-naphthoic acid, m. p. 94°, and 1-naphthol-2-carboxylic acid, m. p. 188°, are simultaneously formed. γ-*o*-Carboxyphenyl-*n*-butyric acid is smoothly hydrogenated in the presence of spongy platinum to γ-o-*carboxy*cyclo*hexyl*-n-*butyric acid*, m. p. 92—94°. 1-Naphthol-2-carboxylic acid is hydrogenated to 1-hydroxy-5 : 6 : 7 : 8-tetrahydronaphthalene-2-carboxylic acid, m. p. 164—165° (cf. Schroeter, A., 1922, i, 130), which is reduced further with difficulty to 1-*hydroxydecahydronaphthalene*-2-*carboxylic acid*, m. p. 167—168°. Catalytic hydrogenation of ethyl 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylate gives a mixture of ethyl decahydronaphthalene-2-carboxylate (cf. Borsche and Lange, this vol., i, 32) and ethyl 1-hydroxydecahydronaphthalene-2-carboxylate; hydrolysis of the latter ester yields 1-*hydroxydecahydronaphthalene*-2-*carboxylic acid*, m. p. 198°. H. W.

Phenylsuccinic Acid Series. VIII. Resolution of *r*-Diphenylsuccinanilic and *r*-Diphenylsuccino-*p*-toluidic Acids into their Optical Antipodes. H. Wren and R. E. Burrows (*J. Chem. Soc.*, 1924, 125, 1934—1937).—*r*-Diphenylsuccinanilic acid has been resolved with quinine, the quinine *l*-diphenylsuccinanilate separating first from alcoholic solutions. l-*Diphenylsuccinanilic acid*, m. p. 193—194° (decomp.), resolidifying and melting again at 224—226°, has $[\alpha]_D^{10\cdot2}$ −338·2° in acetone, $[\alpha]_D^{15}$ −350·3° in ethyl alcohol, and on treatment with alcoholic hydrogen chloride yields l-*diphenylsuccinanil*, m. p. 196—196·5°, $[\alpha]_D^{15\cdot6}$ −117·6° (in chloroform), slight racemisation taking place when the dehydration is effected with acetyl chloride at 40°. On heating at 195°, *l*-diphenylsuccinanilic acid is converted quantitatively into *r*-diphenylsuccinanil (Wren and Williams, T., 1918, **113**, 838). d-*Diphenylsuccinanilic acid* has $[\alpha]_D^{13}$ +337·8° in acetone; d-*diphenylsuccinanil*, m. p. 196—196·5°, has $[\alpha]_D^{17}$ +121·0° in chloroform. *r*-Diphenylsuccino-*p*-toluidic acid was similarly resolved, the quinine salt of the *d*-acid separating in the first fractions (along with racemate). l-*Diphenylsuccino*-p-*toluidic acid*, m. p. 209—209·5°, $[\alpha]_D^{18 \cdot 8}$ −329·5° (in acetone) with alcoholic hydrogen chloride yields l-*diphenylsuccino*-p-*tolil*, m. p. 178°, $[\alpha]_D^{16 \cdot 4}$ −131·5° (in acetone), $[\alpha]_D^{16 \cdot 4}$ −136·3° (in chloroform), which shows a similar change of crystalline form to the *r*-tolil (Wren and Williams, *loc. cit.*). d-*Diphenylsuccino*-p-*toluidic acid* has $[\alpha]_D^{16}$ +330·0° in acetone. d-*Diphenylsuccino*-p-*tolil*, $[\alpha]_D^{15}$ +131·3°, is rapidly racemised by traces of alkali. As with the active diphenylsuccinic anhydrides (Wren and Still, T., 1915, **107**, 1457), the specific rotations of the active anils and tolils are much lower than those of the acids from which they are derived. R. B.

Diphenic Acid Series. II. H. W. Underwood, jun., and E. L. Kochmann (*J. Amer. Chem. Soc.*, 1924, **46**, 2069—2078; cf. this vol., i, 176).—The transformation of diphenic acid or its anhydride into fluorenone-4-carboxylic acid previously described is a general reaction for diphenic acid derivatives containing no substituents in the rings. On heating with sulphuric acid, the dichloride, diamide, diethyl ester, dimethyl ester, monoethyl ester, monomethyl ester, monoamide, and imide (obtained by heating the monoamide with glacial acetic acid and acetic anhydride at 130—140°) of diphenic acid are converted into the corresponding fluorenone-4-carboxylic acid derivatives, but hydrolysis occurs in every case, and no conclusions could be drawn regarding the lability of the groups in the side-chains of the diphenic acid derivatives. Isomerisation of phenanthridone does not take place under these conditions, and *pp'*-dinitrophenic acid, which does not form an anhydride, gives no ketone acid, facts which suggest a *trans*-structure for the dinitro-acid (annexed formula), and also that the meta-orientating nitro group loosens the hydroxyl in the carboxyl group (since *m*-nitrobenzoyl chloride is more reactive than benzoyl chloride) and strengthens the bond holding the hydrogen atom in the latter group as well as that holding the ring hydrogen meta to the nitro group.



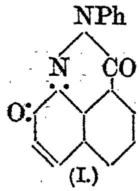
Phenoldiphenein is not isomerised by heat or fuming stannous chloride, but carbon dioxide is evolved at 260—270°. Phenoldiphenein does not give an oxime under the conditions employed for phenolphthalein. In the oxidation of phenanthrene with sodium or potassium dichromate and sulphuric acid, the maximum yield (56%) of phenanthraquinone was obtained with a 350% excess of potassium dichromate. Oxidation of phenanthraquinone gave a maximum yield of diphenic acid (76%) with a 750% excess of potassium dichromate in glacial acetic acid. R. B.

Dipheneins from Resorcinol and Substituted Diphenic Anhydrides. Structure of certain Diphenyl Derivatives. H. Adkins, E. F. Steinbring, and (Miss) E. Pickering (*J. Amer. Chem. Soc.*, 1924, **46**, 1917—1924; cf. A., 1923, i, 578).—Anhydrides of substituted diphenic acids may be prepared when acetamido groups are present in the 4 : 4′- or 6 : 6′-positions, but not when the substituents are nitro or hydroxy groups. The views of various investigators as to the reason for this are discussed. The formation or non-formation of anhydrides is apparently dependent on whether the substituents cause the diphenyl rings to be superimposed or extended (cf. Kaufler, A., 1907, i, 307). The rings are apparently superimposed in the case of diphenic acid and of the amino derivatives of diphenyl but are extended in the case of the nitro or hydroxy derivatives. The 4 : 4′-diaminodiphenic acid, m. p. 250—251°, of Hummel, is shown to be impure. A method is described which furnishes the hydrochloride in fine, white needles, and the free acid as a white solid of m. p. 265°. 4 : 4′-*Diacetamidodiphenic anhydride*, white needles which do not melt, is prepared by refluxing the above hydrochloride with acetic anhydride. Heating with ammonia converts it into 4 : 4′-*diacetamidodiphenamic acid*, $C_{18}H_{17}O_5N_3$. Treatment with sodium hypobromite transforms the last into 2 : 7-*diacetamidophenanthridone*,  $\overset{\text{CO}-\text{NH}}{\text{NHAc}\cdot\text{C}_6\text{H}_3\cdot\text{C}_6\text{H}_3\cdot\text{NHAc}}$, which darkens but does not melt at 350°. 4 : 4′-Diaminodiphenic acid forms a *tetrazonium chloride*, which on hydrolysis gives 4 : 4′-dihydroxydiphenic acid, pure white crystals, m. p. 278° (Schmidt and Scholl describe it as yellow, m. p. 271—272°). 6 : 6′-*Diaminodiphenic acid hydrochloride*, prepared by reducing the corresponding dinitro derivative, forms white crystals; the free *acid* has m. p. 312—313° (decomp.). 6 : 6′-*Diacetamidodiphenic anhydride* is much less stable than the 4 : 4′-isomeride and readily forms the acid on exposure to moisture. Condensation of these substituted anhydrides with resorcinol in the presence of zinc chloride at 110° results in dipheneins. When higher temperatures are employed, the 4 : 4′-diacetamidodiphenic anhydride appears to change to the isomeric fluorenone-4-carboxylic acid, which condenses to form a fluorescein derivative having a free carboxyl group. This rearrangement is not possible in the case of the 6 : 6′-derivative. All these condensation products are fluorescent, although not so markedly as fluorescein. The *condensation product* of 4 : 4′-diacetamidodiphenic anhydride and resorcinol at 110° is a light red powder, which dissolves in dilute alkali to a reddish-brown solution with green fluorescence. On acetylation with boiling acetic anhydride, a dark red solid is obtained, insoluble in sodium carbonate solution. Similar acetylation of the condensation product made at 160—180° gives a *substance*, $C_{40}H_{32}O_{12}N_2$, soluble in sodium carbonate. Condensation of the 6 : 6′-derivative with resorcinol at 110° gives a similar fluorescent product which after acetylation is insoluble in sodium carbonate solution. A *tetrabromo* compound, $C_{30}H_{18}O_7N_2Br_4$, was prepared from a condensation product of the 4 : 4′-anhydride at 135—150°; it forms a red, amorphous powder. The results obtained by Underwood and Kochmann (this vol., i, 176) are criticised. A. C.

The Three Isomeric Naphthol-1 : 8-dicarboxylic Acids and their Azo Derivatives. Abnormal Coupling Reactions in the Naphthalene Series.

K. Dziewoński and T. Stolyhwo (*Ber.*, 1924, **57**, [*B*], 1540—1546).—4- and 2-Naphthol-1 : 8-dicarboxylic acids are distinguished from the 3-hydroxy compound by the marked mobility of the carboxyl group in the ortho or para position to the hydroxyl; this suffers replacement during coupling with diazonium chlorides.

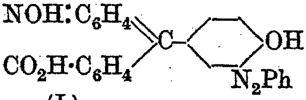
2-*Naphthol*-1 : 8-*dicarboxylic anhydride*, m. p. 350—351°, is prepared by fusing 2-sulphonaphthalene-1 : 8-dicarboxylic acid (cf. Dziewoński and Stolyhwo, this vol., i, 1178) with potassium hydroxide. Its constitution is established by its difference from the other two known naphtholdicarboxylic acids. It couples with benzenediazonium chloride in weakly alkaline solution to form 8-benzeneazo-7-naphthol-1-carboxylic acid, which is isomerised by warm acids into the quinonehydrazone form and thence into 1 : 8-*phenylpyridazone-2-naphthaquinone* (I), m. p. 201—202°; the latter substance is reconverted into 8-benzeneazo-7-naphtholcarboxylic acid by treatment with alkali hydroxide. 4-Naphthol-1 : 8-dicarboxylic acid and benzenediazonium chloride yield 8-benzeneazo-5-naphthol-1-carboxylic acid, which is transformed by acids into 1 : 8-*phenylpyridazone-4-naphthaquinone*, m. p. 238—240°. 3-Naphthol-1 : 8-dicarboxylic acid, on the other hand, couples normally with benzenediazonium chloride, yielding 4-*benzeneazo-3-naphthol*-1 : 8-*dicarboxylic anhydride*, m. p. 260—261°. H. W.



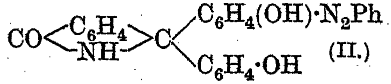
(I.)

Phthaleins. V. Constitution of the Oximic and Iminic Compounds of Phenolphthalein.

B. Oddo and D. Curti (*Gazzetta*, 1924, **54**, 572—581).—Coupling with diazonium salts having proved of advantage in determining the structure of the phthaleins (A., 1913, i, 1110; 1916, i, 87), this method is now applied to the oxime and imide of phenolphthalein. Into the former it is found possible to introduce only one azo group, whereas the imide gives both mono- and bis-azo compounds. This difference in behaviour is regarded as due to the structure being respectively quinonoid and lactoid in the two cases, the azo compounds having the following formulæ :

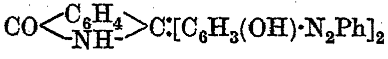


(I.)



$$\mathrm{CO}\!<\!\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{NH}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{C_6H_4(OH)\cdot N_2Ph}\\ \mathrm{C_6H_4\cdot OH}\end{matrix}$$

(II.)

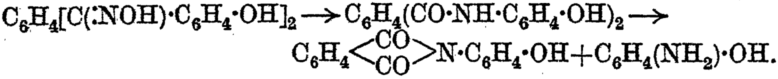


$$\mathrm{CO}\!<\!\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{NH}\end{matrix}\!>\!\mathrm{C{:}[C_6H_3(OH)\cdot N_2Ph]_2}$$

(III.)

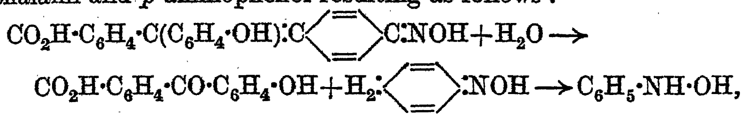
which are in agreement with the formation of a diacetyl compound by the first, and of a triacetyl compound by each of the last two.

When prepared in the ordinary way, phenolphthaleinoxime is always accompanied by *p*-hydroxyphthalanil (cf. Piutti, A., 1886, 1026), which Meyer (A., 1899, i, 707) obtained by the action of excess of hydroxylamine hydrochloride on the oxime in aqueous alcoholic solution and regarded as formed by way of the dioxime, in accordance with the scheme :

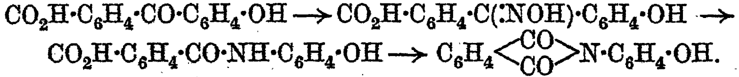


$$C_6H_4[C(:NOH)\cdot C_6H_4\cdot OH]_2 \rightarrow C_6H_4(CO\cdot NH\cdot C_6H_4\cdot OH)_2 \rightarrow C_6H_4{<}{}^{CO}_{CO}{>}N\cdot C_6H_4\cdot OH + C_6H_4(NH_2)\cdot OH.$$

Since this reaction does not take place when free hydroxylamine is used in place of its hydrochloride, the author considers that the hydrochloric acid first effects hydrolysis, the formation of *p*-hydroxyphthalanil and *p*-aminophenol resulting as follows :

(1) 

which undergoes ready isomerisation into *p*-aminophenol.

(2) 

$$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot OH \rightarrow CO_2H\cdot C_6H_4\cdot C(:NOH)\cdot C_6H_4\cdot OH \rightarrow CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot OH \rightarrow C_6H_4{<}{}^{CO}_{CO}{>}N\cdot C_6H_4\cdot OH.$$

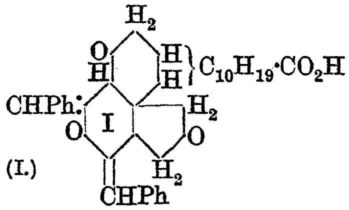
The fact that dichlorophenolphthalein yields, not a bisazo, but only a monoazo compound (cf. Consonno and Apostolo, A., 1921, i, 346), may be due to the presence of the two chlorine atoms; it cannot, therefore, be taken as a proof of the quinonoid constitution of phenolphthalein and its salts.

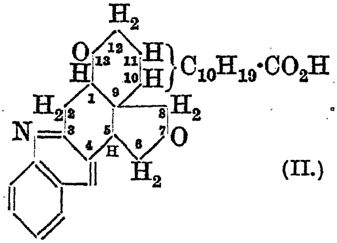
Benzeneazophenolphthaleinoxime, I, m. p. 202°, forms a *diacetyl* compound, m. p. 231—233°. Treatment of the oxime with excess of benzenediazonium chloride results in the formation of a yellow, crystalline *compound*, m. p. 230—231°. *Benzeneazophenolphthaleinimide*, II, pale yellow crystals, has m. p. 248—250°, and its *triacetyl* derivative, orange-yellow crystals, m. p. 183°. *Bisbenzeneazophenolphthaleinimide*, III, forms small, brownish-yellow crystals, m. p. 270—272°, and its *triacetyl* derivative, a brown, crystalline powder, m. p. 207—208°. T. H. P.

Bile Acids. VI. Condensation of some Ketonic Acids of the Cholic Acid Group with Aromatic Aldehydes and with Isatin. W. Borsche and R. Frank (*Ber.*, 1924, 57, [*B*], 1373—1380).—Condensation between aldehydes and certain acids of the cholic acid group occurs only when the carbonyl group is present in ring I (see formula) and the number of aldehyde residues entering the molecule does not exceed the number of methylene groups vicinal to the ketonic group. The failure of similar groups present in other rings to give a similar reaction is not explained. Analogously, condensation with *o*-aminobenzaldehyde or isatic acid to derivatives of quinoline occurs only when the group $\cdot CO\cdot CH_2\cdot$

is present in ring I. Further examples are thus afforded of the failure of "typical" reactions when applied to complex compounds.

Dehydrocholic acid is converted by benzaldehyde in the presence of aqueous sodium hydroxide into *dibenzylidenedehydrocholic acid* (+H_2O) (I), m. p. above 195°. *Dianisylidenedehydrocholic acid* is also described. With *o*-aminobenzaldehyde dehydrocholic acid yields 7 : 13-*diketo*-3 : 4(2′ : 3′)-*quinocholanic acid* (II), m. p. 296° (the corresponding *hydrochloride*, m. p. 264° after softening at 208°, *methyl* ester, m. p. 215°, and *dioxime*, m. p. 317°, are described), whereas with isatin it gives 7 : 13-*diketo*-4-*carboxy*-3 : 4(2′ : 3′)-*quinocholanic acid*, m. p. 297° (decomp.) after previous darkening and softening [*dimethyl* ester; *monoxime*, m. p. 299° (decomp.); *monosemicarbazone*, m. p. 298° (decomp.)]. Dehydrodeoxycholic acid yields *dibenzylidenedehydrodeoxycholic acid*, $C_{38}H_{44}O_4,2H_2O$, m. p. (indefinite) above 95°, *di*-p-*chlorobenzylidenedehydrodeoxycholic acid*, 7-*keto*-3 : 4(2′ : 3′)-*quinocholanic acid*, m. p. 253°, and 7-*keto*-4′-*carboxy*-3 : 4(2′ : 3′)-*quinocholanic acid*, m. p. 298°. 7 : 13-Diketocholanic acid could not be caused to react with benzaldehyde, anisaldehyde, *p*-chlorobenzaldehyde, *o*-aminobenzaldehyde, or isatin, whilst bilianic or deoxybilianic acid did not condense with benzaldehyde, anisaldehyde, *o*-aminobenzaldehyde, or isatin. Pyrodeoxybilianic acid (cf. Wieland and Kulenkampff, A., 1921, i, 112) gives *benzylidenepyrodeoxybilianic acid*, $C_{30}H_{38}O_4$, m. p. 244—245° (+$CH_3\cdot CO_2H$, m. p. 238°), *anisylidinepyrodeoxybilianic acid*, m. p. 270° after softening at 265°, p-*chlorobenzylidenepyrodeoxybilianic acid*, m. p. 282—284° after darkening at 260°, and p-*nitrobenzylidenepyrodeoxybilianic acid*, m. p. 296° (decomp.). *Pyro*iso*deoxybilianic acid* yields *anisylidenepyro*iso*deoxybilianic acid*, $C_{31}H_{40}O_5$, m. p. 181°, and p-*nitrobenzylidinepyro*iso*deoxybilianic acid*, m. p. indefinite, 150—190°. H. W.



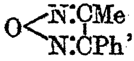


Constitution of the Bile Acids. VII. A Ketone, $C_{22}H_{32}O$, from Deoxybilianic Acid. W. BORSCHE (*Ber.*, 1924, 57, [*B*], 1435—1436).—Distillation of deoxybilianic acid under 10—15 mm. pressure yields pyrodeoxybilianic acid (cf. Wieland and Kulenkampff, A., 1921, i, 112) and small quantities of a *ketone*, $C_{22}H_{32}O$, m. p. 143°. The latter substance combines with bromine, gives an *oxime*, m. p. 169—170°, and a 2-*nitro*-4-*cyanophenylhydrazone*, m. p. 258—259° (decomp.). The *anisylidene* derivative has m. p. 215—219°. H. W.

Constitution of the Bile Acids. VIII. Acylation of Cholic Acid. W. Borsche [with R. Franck, O. Weickert, and F. Hallwass] (*Ber.*, 1924, **57**, [*B*], 1620—1622).—Triacetylcholic acid, $C_{30}H_{46}O_8$, m. p. 257° (cf. Wieland and Boersch, A., 1921, i, 178) is prepared in 30—35% yield by the action of acetyl chloride on a solution of cholic acid in glacial acetic acid; the *methyl* ester has m. p. 180—181°. Acylation of cholic acid in the presence of pyridine gives mainly monoacyl derivatives even when an excess of the reagent is used. The following compounds are described: *methyl* 3-*carbethoxycholate*, m. p. 147°, which is oxidised by chromium trioxide in acetic acid solution to *methyl carbethoxyreductodehydrocholate*, m. p. 125°; *methyl* 3-*anisoylcholate*, m. p. 188°; *methyl* 3-p-*nitrobenzoylcholate*, m. p. 217—218°, and thence *methyl* p-*nitrobenzoylreductodehydrocholate*, m. p. 191—192°. H. W.

Dioximes. XIX. L. Avogadro (*Gazzetta*, 1924, **54**, 545—550).—Since the addition of ammonia or aniline to the oxides of the nitriles of α-oximino-acids, $NOH\colon CR\cdot CNO$, yields the labile forms of aminoglyoximes, $NOH\colon CR\cdot C(NH_2)\colon NOH$, or phenylaminoglyoximes, $NOH\colon CR\cdot C(NHPh)\colon NOH$ (A., 1923, i, 472, 855), the action of magnesium methyl iodide on these nitrile oxides should give the analogous forms of the methylglyoximes. The existence of a labile form of phenylmethylglyoxime (cf. A., 1923, i, 1137; this vol., i, 294) may therefore be expected. Such a labile α-phenylmethylglyoxime is formed by reducing phenylmethylglyoxime peroxide by means of zinc dust and acetic acid, but, owing to the readiness with which it undergoes isomerisation into the ordinary or β-form, it is best prepared as nickel compound by treating the reduced peroxide in alcoholic solution with nickel acetate and ammonia solutions, the nickel being eliminated by means of dilute hydrochloric acid in presence of ether.

Stable or β-phenylmethylglyoxime forms a *diacetyl* compound, $NOAc\colon CMe\cdot CPh\colon NOAc$, m. p. 88—89°, and a *dibenzoyl* compound, m. p. 171°. α-*Phenylmethylglyoxime*, m. p. 140—141°, is converted into the β-form by traces of extraneous substances or, more rapidly, by heating either alone above its melting point or with dilute acetic acid. It dissolves without coloration in dilute sodium hydroxide solution, and is reprecipitated unchanged by carbon dioxide. Concentrated sulphuric acid converts it into the anhydride, *phenylmethylfurazan*,



$O<\begin{array}{l}N\colon CMe\\ \quad|\\ N\colon CPh\end{array}$, a colourless liquid heavier than water and of characteristic odour. When treated either with nitrogen peroxide or with sodium hypochlorite in sodium hydroxide solution, it undergoes dehydrogenation to phenylmethylglyoxime peroxide. The *nickel* compound, probably $C_9H_8O_2N_2Ni$, forms a yellowish-green precipitate but was not obtained pure. The *diacetyl* derivative has m. p. 100—101° with previous softening, and the *dibenzoyl* derivative, m. p. 120°.

T. H. P.

Dioximes. XX. G. Ruggeri and G. Rigoli (*Gazzetta*, 1924, **54**, 550—556).—In view of the fact that the two forms of phenylglyoxime behave differently towards nitrogen peroxide, concentrated sulphuric acid, diazonium salts, nickel, copper, and cobalt salts, etc., diversity in their behaviour towards reducing agents also is to be expected (cf. A., 1923, i, 471, 856); since only the β-modification is a true dioxime, this alone should yield phenylethylenediamine on reduction. Feist and Arnstein (A., 1895, i, 274) obtained this diamine by the action of sodium and alcohol on phenylglyoxime, but the latter probably consisted of a mixture of the α- and β-forms, and the product obtained differs from Purgotti's so-called phenylethylenediamine, formed by the action of zinc and hydrochloric acid on ω-cyanobenzylamine (A., 1895, i, 345). The authors find that this amine is not reducible under such conditions, so that the benzoyl compound and chloroplatinate described by Purgotti are not derivatives of phenylethylenediamine. When heated with either sodium and alcohol or hydriodic acid and red phosphorus, ω-cyanobenzylamine yields ammonia, hydrocyanic acid, benzaldehyde, and other products not identified; with sodium amalgam in aqueous alcoholic solution kept neutral by means of acetic acid, traces of phenylethylenediamine are obtainable, but, in the cold, aluminium amalgam in ethereal solution, stannous chloride and hydrochloric acid, or red phosphorus and hydriodic acid are without sensible action.

Either modification of phenylglyoxime yields phenylethylenediamine when treated with sodium in alcoholic solution, but benzoyl cyanide oxime is probably formed as an intermediate product. By hydriodic acid and red phosphorus, both forms of the glyoxime are converted into ω-aminoacetophenone, which is formed also from benzoyl cyanide oxime under the same conditions; the use of this reducing agent with oximino compounds is preferable to that of others as it furnishes directly hydriodides of amino derivatives, these being sparingly soluble and readily separable. Reduction of both α- and β-phenylglyoxime in ethereal solution by means of aluminium amalgam gives diphenylpyrazine, which is a product of the condensation of ω-aminoacetophenone; similar reduction of benzoyl cyanide oxime gives cyanobenzylamine.

ω-Aminoacetophenone phenylhydrazone, $NH_2 \cdot CH_2 \cdot CPh:N_2HPh$, has m. p. 153° (slight decomp.), and *benzoyl-ω-aminoacetophenone*, $NHBz \cdot CH_2Bz$, m. p. 125°.

Cyanobenzylamine forms a *picrate*, $NH_2 \cdot CHPh \cdot CN, C_6H_3O_7N_3$, m. p. 160—161° (decomp.), and a *benzoyl* derivative, m. p. 159—160°. T. H. P.

s- and as-Dimethyl[cyclo]pentanones. A. Haller and R. Cornubert (*Compt. rend.*, 1924, **179**, 315—320).—In continuation of previous work (cf. A., 1914, i, 291; also A., 1923, i, 92 for complete list of papers) it is confirmed that the dimethyl*cyclo*pentanone obtained by the alkylation of 1-methyl*cyclo*pentan-5-one is the unsymmetrical ketone by the preparation both of the symmetrical 1 : 4-dimethyl*cyclo*pentan-5-one from *ethyl* 1 : 4-*dimethyl*cyclo*pentan-5-one-4-carboxylate*, b. p. 121°/32 mm., d_4^{15} 1·0157, n_D^{15} 1·4431 (the preparation of which from ethyl *cyclo*pentanonecarboxylate is outlined), and of the unsymmetrical 1 : 1-dimethyl*cyclo*pentan-5-one obtained by Blanc (A., 1908, i, 654); and by the preparation of their oximes, semicarbazones, and benzylidene derivatives. The physical constants of the two dimethyl ketones have been redetermined; the 1 : 1- has b. p. 143—144° (corr.)/740 mm., $d_4^{19\cdot5}$ 0·8938, n_D 1·4322; the 1 : 4-, b. p. 147°/744 mm., $d_4^{17\cdot5}$ 0·8918, n_D 1·4312. Condensed with benzaldehyde in the presence of hydrochloric acid the symmetrical ketone yields a *compound* $C_{21}H_{22}O_2$, m. p. 129·5°, obtained by the loss of 1 mol. of water from 2 mols. of benzaldehyde and 1 mol. of ketone; it is the lower homologue of the corresponding *cyclo*hexanone compound, $C_{22}H_{24}O_2$ (cf. A., 1920, i, 390). The unsymmetrical ketone yields benzylidene-1 : 1-dimethyl*cyclo*pentan-5-one, m. p. 36°, together with a brown, viscous residue having a b. p. corresponding with that of the compound, $C_{21}H_{22}O_2$. The oxime of 1 : 4-dimethyl*cyclo*pentan-5-one is an uncrystallisable liquid, b. p. 11·5°/33 mm., and has a camphor-like odour when hot; that of the unsymmetrical ketone has m. p. 65·5° (Blanc, *loc. cit.*, gives 69°). A study of the semicarbazone of the product of alkylation of 1-methyl*cyclo*pentan-5-one shows that this consists mainly of the 1 : 1-dimethyl- together with a small quantity of the 1 : 4-dimethyl-*cyclo*pentan-5-one. J. W. B.

Conversion of Hydroaromatic into Aromatic Compounds. I. Action of Chlorine on 5-Chloro-1 : 1-dimethyl-Δ⁴-*cyclo*hexen-3-one. L. E. Hinkel (*J. Chem. Soc.*, 1924, **125**, 1847—1855).—The difference between the action of chlorine and bromine on the same hydroaromatic compound previously recorded (T., 1920, **117**, 1296) has now been observed in the case of 5-chloro-1 : 1-dimethyl-Δ⁴-*cyclo*hexen-3-one (cf. Crossley and Renouf, T., 1914, **105**, 169), which on treatment with chlorine in cold chloroform solution yields 4 : 5-*dichloro*-1 : 1-*dimethyl*-Δ⁵-cyclo*hexen*-3-*one*, a liquid with a camphoraceous odour, b. p. 120—121°/13 mm. The dichloroketone on heating loses hydrogen chloride and is converted into 5-chloro-*o*-3-xylenol (Hinkel and others, T., 1923, **123**, 2968). Alcoholic potassium hydroxide converts it into the same compound, whilst on heating with sulphuric acid 6-*chloro*-o-4-*xylenol*, m. p. 98° (*benzoate*, m. p. 42°), is obtained. The structure of the last is established by its synthesis from 5-nitro-*o*-3-xylidine, which is converted by the diazo reaction into 6-*chloro*-4-*nitro*-o-*xylene*, m. p. 101°, giving on reduction 6-*chloro*-o-4-*xylidine*, m. p. 72°, from which 6-chloro-*o*-4-xylenol is obtained by diazotisation of the sulphate. On treatment of the dichlorohexenone with chlorine in chloroform solution there is obtained 3 : 4 : 5-*trichloro*-1 : 1-*dimethyl*-Δ⁴-cyclo*hexen*-3-*one*, m. p. 61°, the main product of the action of chlorine on 5-chloro-1 : 1-dimethyl-Δ⁴-*cyclo*hexen-3-one at the ordinary temperature. On treatment with alcoholic potassium hydroxide, the trichlorohexenone yields 4-*chloro*-3 : 5-*dihydroxy*-o-*xylene*, m. p. 123° (*dibenzoate*, m. p. 137°); sulphuric acid converts it into 5 : 6-*dichloro*-o-4-*xylenol*, m. p. 102° (*benzoate*, m. p. 94°), which with chlorine in light petroleum yields the *trichloro*-o-4-*xylenol*, m. p. 182·5° (*benzoate*, m. p. 120°), obtained by the action of chlorine on 6-chloro-*o*-4-xylenol; whilst on heating with quinoline at 170°, 4 : *5-dichloro-*o*-3-xylenol*, m. p. 95° (*benzoate*, m. p. 128°, *tetrachloro* derivative, $C_8H_6OCl_4$, m. p. 127·5°), is obtained.

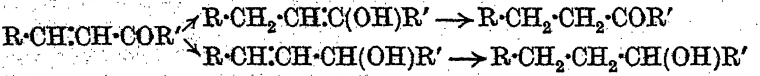
The liquid from which the trichlorohexenone separates on distillation yielded a fraction, b. p. 145—155°/13 mm., from which 2 : 4 : 5 : *6-tetrachloro-*1 : 1-*dimethyl*cyclo-Δ^4-*hexen-3-one*, m. p. 91°, was obtained, probably formed from the dichloroketone by chlorination and loss of hydrogen chloride, since the trichloroketone is not further attacked by chlorine in boiling chloroform solution. On treatment with alcoholic potassium hydroxide, the tetrachloroketone yields a *dichloroxylenol*, $C_8H_8OCl_2$, m. p. 119—120° (*benzoyl* derivative, m. p. 129°), whilst with sulphuric acid a mixture of trichloro-*o*-3- and -*o*-4-xylenols is obtained. R. B.

Phenyl γ-Chloropropyl Ketone. J. B. Conant, J. B. Segur, and W. R. Kirner (*J. Amer. Chem. Soc.*, 1924, **46**, 1882—1885).—The ketone was synthesised from trimethylene glycol in the following steps: $OH\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH \rightarrow CH_2Cl\cdot CH_2\cdot CH_2\cdot OH \rightarrow CH_2Cl\cdot CH_2\cdot CH_2Br \rightarrow CH_2Cl\cdot CH_2\cdot CH_2\cdot CN \rightarrow CH_2Cl\cdot CH_2\cdot CH_2\cdot COPh$. The yields for successive steps were 65%, 70%, 42%, and 50%, giving an over-all yield on the glycol of about 9% of the theoretical. *Phenyl γ-chloropropyl ketone*, m. p. 19—20°, prepared by the interaction of ethereal solutions of γ-chlorobutyronitrile and magnesium phenyl bromide at 0°, has no lachrymatory properties, in contrast to the α-chloroketones. The best method of identifying the ketone is through its condensation product with phenylhydrazine, 1 : 3-*diphenyltetrahydropyridazine*, $\overline{\text{NPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}{:}\text{CPh}\cdot\text{N}}\text{H}$, m. p. 138—139°. Benzoyl*cyclo*propane was obtained in good yield by the action of potassium hydroxide in methyl alcohol on the ketone at the ordinary temperature; the tendency to form this *cyclo*propane may account for the low yield in the last step of the synthesis. A. C.

***CC*-Phenylalkylmethane Dialkylsulphones.** Chemische Fabrik von Heyden Akt.-Ges. (D.R.-P. 376472; from *Chem. Zentr.*, 1924, i, 965).—The sulphones described are obtained by condensing ketones with alkylmercaptans and oxidising the resulting mercaptols. The following compounds are mentioned: *αα-diethylthiol-α-phenylpropane*, $CPhEt(SEt)_2$, a light yellow oil, which on oxidation yields *αα-diethylsulphone-α-phenylpropane*, $CPhEt(SO_2Et)_2$, crystals, m. p. 115—116°; *αα-diethylsulphone-α-phenyl-Δγ-butylene*, crystals, m. p. 136—138°. G. W. R.

Indene Series. F. Ishiwara (*J. pr. Chem.*, 1924, [ii], **108**, 194—199).—2-Bromo-1-hydroxyhydrindene is obtained by boiling indene dibromide with magnesium carbonate in aqueous acetone (cf. Krämer, A., 1891, 205). It is oxidised by dichromate and sulphuric acid to 2-bromo-1-hydrindone, which decomposes explosively at 152°. When boiled with sodium acetate in glacial acetic acid, the latter affords 2-*acetoxy*-1-*hydrindone*, b. p. 128°/0·1 mm., 137°/1·0 mm., 165°/17 mm., 172°/19 mm., which reduces cold Fehling's solution, and is hydrolysed by potassium carbonate in aqueous methyl alcohol to *2-hydroxy-1-hydrindone*, m. p. 40—40·5° (sinters at 38°), b. p. 95°/0·05 mm., 128—133°/1 mm., which also reduces Fehling's solution, and decomposes on keeping; the *phenylurethane* has m. p. 133—134° after sintering at 129°. It yields 1 : 2-diketohydrindene (cf. T., 1912, **101**, 232) on oxidation with chromic acid, and the *osazone* of this diketone, m. p. 222—223° (cf. Gabriel, A., 1897, i, 61), together with the *substance* $C_{15}H_{14}ON_2$, m. p. 123—124°, on treatment with phenylhydrazine. F. G. W.

Formation of Alcohols and Hydrocarbons by the Catalytic Hydrogenation of Aromatic and Aliphatic–Aromatic Carbonyl Compounds. F. Straus and H. Grindel (*Annalen*, 1924, **439**, 276—312).—The products of hydrogenation of several carbonyl compounds in acetone solution by means of palladium and hydrogen at the ordinary temperature and pressure, have been examined. Only those compounds in which the carbonyl group is in the α-position to the benzene ring can be ultimately reduced to the saturated hydrocarbon, the other carbonyl compounds being reduced to the carbinol. The stages of the reduction may be followed graphically in some cases, by the different rates of absorption of hydrogen. This method of preparation of some of the intermediate reduction products is superior to other reduction methods, for example, the preparation of αγ-diphenylpropyl alcohol. In some cases, mixtures are produced, especially where addition of hydrogen may take place at the 1 : 2- or 1 : 4-positions. Styryl methyl ketone and distyryl ketone, for instance, are only partly reduced to the corresponding carbinols :



$$R\cdot CH{:}CH\cdot COR' \begin{cases} \nearrow R\cdot CH_2\cdot CH{:}C(OH)R' \longrightarrow R\cdot CH_2\cdot CH_2\cdot COR' \\ \searrow R\cdot CH{:}CH\cdot CH(OH)R' \longrightarrow R\cdot CH_2\cdot CH_2\cdot CH(OH)R' \end{cases}$$

and the methoxyl derivatives behave similarly.

Phenyl styryl ketone on reduction yields progressively, phenyl β-phenylethyl ketone, αγ-diphenylpropyl alcohol, and αγ-diphenylpropane. *p*-Anisyl *p*-methoxystyryl ketone yields p-*anisyl* β-p-*methoxyphenylethyl ketone*, m. p. 42—43° (*oxime*, m. p. 116—118·5°, *semicarbazone*, m. p. 148—149°), and finally *αγ-di*-p-*methoxyphenylpropane*, m. p. 45—46°. With 2 mols. of hydrogen a mixture of the saturated ketone, carbinol, and hydrocarbon are produced. Acetophenone yields phenylmethylcarbinol and, more slowly, ethylbenzene, whilst the *p*-methoxy derivative yields a mixture of acetylanisole, anisylmethylcarbinol, and ethylanisole. Benzophenone yields benzhydrol and, finally, diphenylmethane, whilst *pp*-dimethoxybenzophenone with 1 mol. of hydrogen yields a mixture of the ketone and dianisylmethane. Styryl methyl ketone yields phenylethyl methyl ketone, and the *p*-methoxy derivative yields a mixture of *p*-methoxyphenylethyl methyl ketone and δ-*p*-methoxyphenylbutan-β-ol. Phenyl propenyl ketone gives progressively, phenylpropylcarbinol, m. p. 14·5°, and *n*-butylbenzene. Distyryl ketone is partly reduced to the corresponding carbinol, and di-*p*-methoxystyryl ketone is more completely reduced to di-*p*-methoxyphenylethyl ketone; the carbinol could not be isolated. Cinnamylideneacetophenone gave αε-diphenylpentane in good yield.

Cinnamaldehyde on exhaustive hydrogenation yielded a mixture of hydrocinnamaldehyde and propylbenzene; with 1 mol. of hydrogen, it gave a mixture of propylbenzene, hydrocinnamyl alcohol, and unchanged aldehyde. Cinnamyl alcohol gave the saturated alcohol and a small amount of the hydrocarbon. By exhaustive hydrogenation of cinnamaldehyde by Skita's method in alcoholic solution, the saturated alcohol was the chief product, with a little hydrocinnamaldehyde; with 1 mol. of hydrogen, some of the cinnamaldehyde was unchanged.

Benzaldehyde with 2 mols. of hydrogen yields toluene and with 1 mol. a mixture of benzyl alcohol, toluene, and benzaldehyde.

A. E. C.

Use of Aliphatic Acid Anhydrides in the Preparation of Ketones by the Friedel and Crafts Reaction. C. R. NOLLER and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, **46**, 1889—1896).—The poor results obtained by various workers on substituting acetic anhydride for acetyl chloride in the preparation of ketones by the Friedel and Crafts method is due to the fact that only 1 mol. or less of aluminium chloride was employed. Using 2 or more mols. of the latter, the condensations proceed regularly and smoothly and 80—90% of the theoretical yields (calculated on the results of the first distillation of the crude product) are readily obtainable. Some 19 ketones were prepared, and the only variation in conditions found necessary was an occasional change in the temperature or length of time of reaction. In the case of compounds containing alkoxy groups the splitting of the ether linking is less liable to occur than with acetyl chloride, and rarely amounts to more than 5% of the reaction mixture; using anhydrides other than acetic anhydride, it does not occur at all. In the case of *p*-methyl-ω-chloroacetophenone, the yield is comparatively low; it is better in this case to use chloroacetyl chloride than the chloroanhydride. Incidentally, the methoxyacetonaphthene prepared by Fries (A., 1921, i, 423) is shown to be 2-methoxy-α-naphthyl methyl ketone and the following compounds are described: 4-*Methoxy*-3-*methylacetophenone*, m. p. 26—26·5°, b. p. 116°/3 mm., 273·5°/744 mm.; 2-*methoxy*-5-*methylbutyrophenone*, b. p. 123°/3 mm., 276·5°/739 mm., d_4^{20} 1·0258, n_D^{20} 1·5250; 4-*methoxy*-3-*methylvalerophenone*, m. p. 31—33°, b. p. 151·5°/4 mm., 308·7°/744 mm.

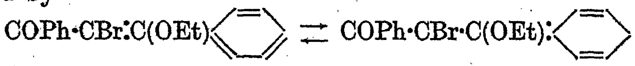
A. C.

Multiple Forms (Pseudopolymorphism) of Derivatives of Phenylethylene, R′R″C:CR‴Ph. A. GILLET (*Bull. Soc. chim. Belg.*, 1924, **33**, 377—388; cf. this vol., i, 651).—Phenyl β-ethoxystyryl ketone, COPhCH:CPh·OEt, when treated with 1 mol. of bromine in carbon disulphide solution at 0°, and then with a solution of anhydrous potassium acetate in absolute alcohol, gives *phenyl* α-*bromo*-ββ-*diethoxy*-β-*phenylethyl ketone*,

$$COPh{\cdot}CHBr{\cdot}CPh(OEt)_2,$$

m. p. 72°, in 90% yield. The latter compound, when heated at

190—200°/3 mm., gives *phenyl α-bromo-β-ethoxystyryl ketone*, $\mathrm{COPh{\cdot}CBr{:}CPh{\cdot}OEt}$ in 70% yield. This compound can be obtained in three isomeric and crystallographically distinct forms, all pale yellow crystals, m. p. (*a*) 64—65°, (*b*) 73°, (*c*) 75·5—76·5°, solubility in methyl alcohol at 18°, (*a*) 17·1, (*b*) 8·5, and (*c*) 6·4%. (*a*) and (*b*) are unstable and change, slowly on keeping and rapidly on seeding, into (*c*). The isomeride (*a*) is formed usually on spontaneous crystallisation of the molten compound, but each of the isomerides can be prepared by seeding the liquid with the required form. The author considers that the existence of two of these isomerides is due to "quinonoid transposition," probably represented by



One of the forms is almost certainly one of two *cis-trans* isomerides and the second geometrical isomeride is being sought. *Phenyl α-bromo-β-methoxystyryl ketone*, prepared similarly to the ethoxy compound, has been obtained in two crystallographically distinct forms, both pale yellow, m. p. (*a*) 63·5—64·5°, (*b*) 71—72°, solubility at 19° in petroleum of b. p. 80—85°, (*a*) 2·84, (*b*) 2·24%, in ethyl alcohol, (*a*) 9·9 at 19°, (*b*) 6·1% at 17°; (*a*) is obtained by spontaneous crystallisation, but is easily converted by seeding into the more stable (*b*); (*a*) can also be obtained by seeding the molten compound with the corresponding isomeride of phenyl dibromo- and di-iodo-styryl ketone. A third (*cis-trans*) isomeride, m. p. 101° (approx.), has been isolated. The isomerides (*a*) and (*b*) of the methoxy compound correspond with (*b*) and (*c*) of the ethoxy compound, respectively. *Phenyl α-bromo-β-propoxystyryl ketone* has been obtained in only one form, m. p. 49°, corresponding with the isomeride (*a*) of the ethoxy compound. Many examples of similar polymorphism already recorded are collected in the paper.

F. G. M.

Correction of the Constitutional Formula of Benzylbenzoin. A. García Banús and J. Pascual Vila (*Anal. Fís. Quím.*, 1924, **22**, 262—263; cf. A., 1922, i, 734).—The product of the reaction of equimolecular portions of magnesium benzyl chloride and benzil, to which the formula $\mathrm{CH_2Ph{\cdot}CPhBz{\cdot}OH}$ was originally assigned, is now shown to be identical with the benzyl ether of benzoin.

G. W. R.

Action of Nitroxyl on α-Ketoaldehydes. IX. Preparation of α-Ketoformhydroxamic Acids. C. Gastaldi (*Gazzetta*, 1924, **54**, 589—592; cf. A., 1923, i, 1236; this vol., i, 733).—The addition of nitroxyl to the α-ketoaldehydes, phenylglyoxal, $\mathrm{Ph{\cdot}CO{\cdot}CH(OH)_2}$, and *p*-tolylglyoxal, $\mathrm{C_6H_4Me{\cdot}CO{\cdot}CH(OH)_2}$, follows the normal course (cf. Angeli, A., 1902, i, 78, 765; 1904, i, 172; 1905, ii, 385). As a reagent for furnishing nitroxyl, benzenesulphonhydroxamic acid yields better results than nitrohydroxylaminic acid. Thus, addition of sodium hydroxide solution to a methyl-alcoholic solution of phenylglyoxal and benzenesulphonhydroxamic acid, cooled in ice, yields almost pure sodium benzoylformhydroxamate.

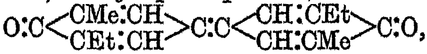
p-*Methylbenzoylformhydroxamic acid*, $C_6H_4Me{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}OH$ or $C_6H_4Me{\cdot}CO{\cdot}C(OH){:}NOH$, prepared from *p*-tolylglyoxal and benzenesulphonhydroxamic acid, has m. p. 112° (decomp.); its *sodium* salt deflagrates when heated. Its *α-oxime*, $C_6H_4Me{\cdot}C({:}NOH){\cdot}CO{\cdot}NH{\cdot}OH$ or $C_6H_4Me{\cdot}C({:}NOH){\cdot}C(OH){:}N{\cdot}OH$, pale red needles, m. p. 186° (decomp.), gives a deep red coloration with ferric chloride; the yellow *nickel* compound is soluble, and the olive-green *copper* compound insoluble, in dilute acetic acid. The *β-oxime*, obtained by heating the α-modification with dilute acetic acid in presence of nickel acetate and decomposing the nickel compound formed by means of dilute sulphuric acid, m. p. 183° (decomp.), gives a violet-red coloration with aqueous ferric chloride; the *nickel* compound is a voluminous, brick-red precipitate, and the *copper* compound an olive-green precipitate.

T. H. P.

Preparation of Higher Ketones. B. HELFERICH and L. KEINER.—(See i, 1166.)

Diphenoquinones. K. VON AUWERS and G. WITTIG (*Ber.*, 1924, **57**, [*B*], 1270—1275).—Monohydric phenols containing substituents in the two ortho positions to the hydroxy group resemble *vic.-m*-xylenol (Auwers and Markovitz, A., 1905, i, 219; 1908, i, 629) in being oxidisable to diphenoquinones if the substituents are alkyl groups, but not if phenyl or chlorine is present. The oxidation is best effected by short, vigorous treatment of the phenols with chromium trioxide in boiling glacial acetic acid solution.

3-*Ethyl*-o-*cresol*, b. p. 91—92°/12 mm. (*phenylurethane*, m. p. 147—148°), prepared by the reduction of 3-acetyl-*o*-cresol with amalgamated zinc and hydrochloric acid, is oxidised to 3 : 3′(3 : 5′)-*dimethyl*-5 : 5′(5 : 3′)-*diethyldiphenoquinone*,



$$O{:}C{<}\begin{matrix}CMe{:}CH\\CEt{:}CH\end{matrix}{>}C{:}C{<}\begin{matrix}CH{:}CEt\\CH{:}CMe\end{matrix}{>}C{:}O,$$

m. p. 153°, which is reduced by zinc dust and dilute acetic acid to 4 : 4′-*dihydroxy*-3 : 3′-*dimethyl*-5 : 5′-*diethyldiphenyl*, m. p. 148° (*dibenzoate*, m. p. 171—172°). 3-Ethyl-*o*-cresol and nitrous acid yield 5-*nitroso*-3-*ethyl*-o-*cresol*, m. p. 135—136°, which is oxidised by potassium ferricyanide to 5-*nitro*-3-*ethyl*-o-*cresol*, m. p. 133—134°.

3-*Propenyl*-o-*cresol*, b. p. 113—115°/12 mm., m. p. 41—42°, obtained by the action of concentrated aqueous potassium hydroxide on 3-allyl-*o*-cresol at 150°, is reduced by sodium and boiling alcohol to 3-*propyl*-o-*cresol*, b. p. 105—107°/12 mm. (*phenylurethane*, m. p. 110—111°). The substance is also prepared by the reduction of 3-*propionyl*-o-*cresol*, b. p. 127—129°/15 mm., m. p. 22—23° (*semicarbazone*, m. p. 202°) by Clemmensen's method, the ketone being obtained together with 5-*propionyl*-o-*cresol*, m. p. 83·5—84°, by the action of aluminium chloride at 120° on o-*tolyl propionate*, b. p. 99°/12 mm. The cresol is transformed by nitrous acid into 5-*nitroso-3-propyl*-o-*cresol*, m. p. 93—94°, and is oxidised by chromic acid to 3 : 3′(3 : 5′)-*dimethyl*-5 : 5′(5 : 3′)-*dipropyldiphenoquinone*, bluish-green crystals, m. p. 136—137°; the latter is reduced to 4 : 4′-*dihydroxy*-3 : 3′-*dimethyl*-5 : 5′-*dipropyldiphenyl*, m. p. 123·5—125° (*diacetate*, m. p. 95—96°).

4-*Chloro-2-ethylphenol*, b. p. 118—119°/12 mm., is converted into the corresponding *acetate*, b. p. 132°/12 mm., which is isomerised by aluminium chloride at 120° to 4-*chloro*-6-*acetyl*-2-*ethylphenol*, b. p. 145—146°/12 mm. (the *sodium* salt and the *semicarbazone*, m. p. 229—230°, are described). The ketone is reduced by zinc and hydrochloric acid to 1-*chloro*-2 : 6-*diethylphenol*, b. p. 128—132°/12 mm., m. p. 31—31·5°, which is converted by sodium and boiling alcohol into 2 : 6-*diethylphenol*, m. p. 37·5—38°. 3 : 5 : 3′ : 5′-*Tetraethyldiphenoquinone* forms bluish-red needles, m. p. 142—143°. H. W.

Naphthaquinone Derivatives. SOCIÉTÉ ANONYME DES MATIÈRES COLORANTES ET PRODUITS CHIMIQUES DE SAINT-DENIS, A. WAHL and R. LANTZ (Brit. Pat. 206142).—A 4-arylamino-1-arylimino-β-naphthaquinone is obtained, together with an equivalent of a 1-arylamino-β-naphthol, by the action of a primary aromatic amine on a 1-arylimino-β-naphthaquinone. By the further action of the same, or another, amine, the 1-arylimino group of the naphthaquinone produced may be replaced, when the aryl radical of the amine is different from that of the 1-arylimino group, by an arylimino group derived from the amine, the 4-arylamino group remaining unattacked. In this way, compounds containing the same or different aryl radicals attached to the 1-imino and 4-amino nitrogen atoms can be prepared. By carrying out the reaction in presence of air and a catalyst such as lime, baryta, or cupric oxide, the 1-arylimino-β-naphthol is reoxidised to the 1-arylimino-β-naphthaquinone, so that the latter under these conditions is completely converted into the 4-arylamino-1-arylimino derivative. The same result is obtained by treating a 1-arylamino-β-naphthol with an amine in presence of air and one of the above catalysts. Under these conditions, the products are isolated as pure crystalline derivatives of the metal present. The 4-arylamino-1-arylimino-β-naphthaquinones are hydrolysed by dilute acids to 4-arylimino-2-hydroxy-α-naphthaquinones and are isomerised when boiled in glacial acetic acid to 2-arylamino-4-arylimino-α-naphthaquinones. 4-*Phenylamino*-1-*phenylimino*-β-*naphthaquinone*, brown-red crystals, 4-p-*toluidino*-1-p-*tolylimino*-β-*naphthaquinone*, brown prisms, 4-*phenylamino*-1-p-*tolylimino*-β-*naphthaquinone*, 4-o-*methoxyphenylamino*-1-o-*methoxyphenylimino*-β-*naphthaquinone*, and the copper compounds of the first and last of these are described. F. G. W.

Isomerism of Menthol and *neo*Menthol. G. VAVON and A. COUDERC (*Compt. rend.*, 1924, **179**, 405—408).—*d*-*neo*Menthol is readily prepared by the reduction of *l*-menthone with hydrogen in the presence of platinum black, using acetic acid, ether, or alcohol as solvent. The velocity of reduction decreases with the solvents in the order named. The separation of the isomerides in the product, ($[\alpha]_{578}$ +4° to +10°) is effected by esterification with succinic anhydride and crystallisation of the *neo*menthyl succinate from aqueous alcohol and aqueous acetic acid to constant rotatory power. d-neo*Menthyl succinate*, m. p. 68°, has $[\alpha]_{578}$ +34·70° (in chloroform), and on hydrolysis yields a *d*-*neo*menthol, b. p. 107—108°/20 mm., d_4^{22} 0·897, n_D^{22} 1·4594, $[\alpha]_{578}$ +21·95° (cf. Pickard and Littlebury, T., 1912, **101**, 109). The velocity of esterification of *neo*menthol with acetic and butyric acids is much less than that of menthol, the difference being more pronounced at lower temperatures and in the presence of a catalyst (hydrochloric acid). Similarly, the hydrolysis of *neo*menthyl hydrogen succinate by alcoholic potassium hydroxide proceeds much more slowly than that of the corresponding menthol ester. These differences, and the preponderating formation of *neo*menthol in the reduction of menthone, are readily explained by the theory of steric hindrance, when *neo*menthol is regarded as the *cis*- and menthol as the *trans*-form of 1-methyl-4-*iso*propylhexan-3-ol.

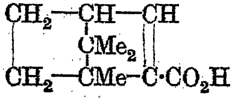
R. B.

Dependence of Optical Rotatory Power on Chemical Constitution. V. Rotatory Dispersions of *d*-Camphorimide, *d*-Camphorbenzylimide, Benzyl-*d*-camphoramic Acid, and their Derivatives. B. K. Singh and A. C. Biswas (*J. Chem. Soc.*, 1924, **125**, 1895—1898).—The rotatory powers of a number of benzyl and substituted benzyl derivatives of *d*-camphorimide and of *d*-camphoramic acid for the wave-lengths 5893, 5780, 5461, have been studied in benzene, ether, chloroform, acetone, ethyl alcohol, and methyl alcohol solution. Substitution of the benzyl group for the imido-hydrogen atom increases the rotatory power. In all cases except camphor-*o*-nitrobenzylimide, the rotatory power is lowest in benzene, which has the lowest dielectric constant, but no regular relation was disclosed between the rotatory powers and the dielectric constants of the other solvents. The rotatory dispersion of *d*-camphorimide and its benzyl derivative is highest in benzene where the rotatory power is lowest, whilst the converse is the case with camphor-*o*-nitrobenzylimide, and it appears that in this series the rotatory power and the rotatory dispersion are influenced in opposite directions by the change from an aliphatic solvent to benzene. The relative magnitude of the rotatory power of camphorbenzylimide and its three nitro derivatives varies with the nature of the solvent. Frankland's rule holds only in chloroform and in benzene, whilst Cohen's rule is valid except in chloroform and in methyl alcohol, the deviation in the latter solvent being very marked. The rotation is increased considerably when the ring structure is opened by hydrolysis, and the following values for $[M]_D$ in ethyl alcohol are given: camphorimide, 10·99°; camphoramic acid, 89·45° (α); 119·4° (β); camphorbenzylimide, 30·19°; benzylcamphoramic acid, 99·88°; camphor-*m*-nitrobenzylimide, 31·92°; 3-nitrobenzylcamphoramic acid, 106·70°.

d-*Camphor*-o-*nitrobenzylimide*, m. p. 131°, from benzyl chloride and camphorimide in alcoholic potassium hydroxide solution, on hydrolysis with potassium hydroxide yields a dark greenish-brown and a brown o-*nitrobenzyl*-d-*camphoramic acid*. d-*Camphor*-m-*nitrobenzylimide*, m. p. 69°, similarly prepared, on hydrolysis yields two colourless m-*nitrobenzylcamphoramic acids*, m. p. 134° and 179°. *d*-Camphor-*p*-nitrobenzylimide similarly yields a brown-orange form, decomp. 250°, and a deep purple-brown form, m. p. above 325°, of p-*nitrobenzoyl*-d-*camphoramic acid*. d-*Benzylcamphoramic acid* has m. p. 149°. R. B.

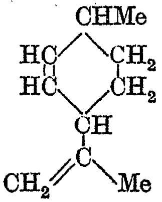
Valency. IV. Absorption Spectra of Camphor, Benzylidenecamphor, and Camphorquinone. Optical Evidence of Two Types of Conjugation. T. M. Lowry and H. S. French (*J. Chem. Soc.*, 1924, **125**, 1921—1927).—Quantitative observations of the absorption spectra of camphor and of camphorquinone in alcohol, benzene, and *cyclo*hexane show that the position of the band is almost independent of the solvent and concentration. On passing from camphor to camphorquinone the band at 2880 Å. (alcoholic solution) is shifted to 4650 Å., whilst the molecular extinction coefficient remains practically constant at $\log \epsilon = 1{\cdot}5$. The development of colour is thus not accompanied by any increase in absorptive power. In benzylidenecamphor, the molecular extinction coefficient becomes $\log \epsilon = 4{\cdot}32$, but the wave-length remains at 2900 Å., being practically unaltered by the extension of the conjugated system. It is concluded that benzylidenecamphor and camphorquinone represent two different types of conjugation, and that some additional factor beyond a long conjugated chain is required to produce visible colour. In the quinones, this may be supplied by the presence of two doubly-linked oxygen atoms at the end of a conjugated chain. R. B.

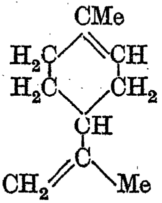
Carbylamines. IX. Reaction of Phenylcarbylamine with Pernitrosocamphor. M. Passerini (*Gazzetta*, 1924, **54**, 540—544).—Phenylcarbylamine and pernitrosocamphor interact slowly in the cold, giving nitrous oxide and *d*-bornylene-6-carboxylic anilide. The acid, formed when the anilide is hydrolysed, rapidly decolorises permanganate, readily unites with bromine, and is reduced to *d*-camphane-6-carboxylic acid by hydrogen in presence of platinum black. d-*Bornylene*-6-*carboxylic acid* (annexed formula), has m. p. 65—66°, $[\alpha]_D^{23 \cdot 5}$ (in ethyl acetate) +66·2°; *anilide*, m. p. 124—125°. d-*Camphane*-6-*carboxylic acid* has m. p. 72—74°, $[\alpha]_D^{26 \cdot 5}$ +11·2°, and yields a sparingly soluble *silver* salt. T. H. P.



Diprene, a new Terpene. O. Aschan (*Annalen*, 1924, **439**, 221—232).—Isoprene (250 g.) was left in an atmosphere of carbon dioxide in a sealed vessel in the dark for 10 years, and then the residual isoprene (76%) was removed. The viscous, rubber-like residue possessed an odour resembling that of rancid olive oil and contained an oil (7·6 g.) volatile in steam. The non-volatile residue on distillation under diminished pressure yielded an oil, b. p. below 80°/7 mm. (7 g.). These two fractions were combined and distilled over sodium under normal pressures, whereby after two distillations, three main fractions were obtained: (1) b. p. 171—172°, d_4^{20} 0·8535 (4·2 g.); (2) b. p. 173—173·5°, d_4^{20} 0·8552 (1·6 g.); (3) b. p. 175·5—178°, d_4^{20} 0·8603 (1·2 g.). The first fraction is a new hydrocarbon, $C_{10}H_{16}$, which the author names *diprene*. It gives no reaction for sylvestrene, and no nitrosite, as does dipentene. It yields a *dihydrochloride*, m. p. 51·5—52°, which has an odour of juniper oil, and is not identical with that obtained from dipentene

(I.)





(II.)

(m. p. 49—50°) or terpinene (m. p. 51—52°). β-Terpinene, which closely resembles diprene in physical properties, yields a crystalline tetrabromide (Wallach, A., 1908, i, 813), but by the action of bromine on an alcoholic solution of diprene at −10°, an oily tetrabromide is formed, stable towards permanganate, which will not crystallise, and may be a mixture of several stereoisomerides.

It is suggested that in the polymerisation of isoprene to form a dimeric compound, a dipentene would be more likely to be formed than a terpinene, at low temperatures, as the former would involve a smaller structural alteration than the latter. The new terpene probably possesses formula I, which isomerises to dipentene (II) on heating or further distillation. The higher boiling fraction (3) probably contains some dipentene, produced by isomerisation, which would account for the fact that the hydrochloride obtained from this fraction is difficult to crystallise. A. E. C.

Heat of Combustion of Natural and "Sulphuric Acid" Caoutchouc. F. Kirchhof and O. Matulke (*Ber.*, 1924, 57, [*B*], 1266—1270).—The heat of combustion of plantation pale crêpe rubber is approximately 10,700 cal. per gram. Its empirical formula is $(C_5H_8)_n$, and is therefore identical with that of Congo and synthetic isoprene caoutchouc. The heat of combustion of "sulphuric acid caoutchouc" (cf. Kirchhof, A., 1921, i, 116; 1922, i, 562) is markedly lower than that of natural rubber and depends on the degree of internal polymerisation. The empirical formula of "sulphuric acid caoutchouc," calculated to ash- and sulphate-free material, corresponds very closely with the expression, $(C_{100}H_{160})_nSO_2$. The action of sulphuric acid on resin-free, natural caoutchouc in different media is accompanied by evolution of heat which is approximately proportional in amount to the content of undissolved caoutchouc; the latter is partly depolymerised and oxidised. The transformation (internal polymerisation) is, however, attended by absorption of heat. H. W.

Caoutchouc. II. Hydrocaoutchouc and a Crystalline Form of Caoutchouc. R. Pummerer and A. Koch (*Annalen*, 1924, **438**, 294—313).—The following procedure affords samples of caoutchouc of progressively increasing purity, all operations being carried out in an inert atmosphere: (*a*) fractional precipitation from benzene by means of alcohol, the impurities containing oxygen being precipitated in the first fraction, and the solvent removed by extraction with acetone; (*b*) as in (*a*) followed by fractional precipitation from hexahydrotoluene by means of acetone; (*c*) treatment of the product from (*b*) in light petroleum solution with methyl-alcoholic potassium hydroxide, the ethereal solution of the product then being shaken with charcoal. The product from (*a*) gives a clear solution in benzene, turbid in hexahydrotoluene, ether, or light petroleum; that from (*b*) is clear in hexahydrotoluene; and that from (*c*) is clear in all four solvents, and sufficiently pure for direct cold catalytic hydrogenation. On cooling the product obtained as in (*a*) after extraction with acetone, crystals were formed in the rubber mass, the occurrence of three types of crystals in six modifications being ascribed to the presence of several chemical individuals in the purified product. The benzene–alcohol mother-liquors deposited, on keeping, further fractions of caoutchouc which gradually set to a mass of yellowish-white, spherical aggregates, non-crystalline material being removable by washing in ether, from which solvent recrystallisation could also be effected. The crystals became transparent and plastic at 60°, complete fusion taking place at 92°. The sample became partly isotropic at 44°, completely isotropic at 60—62°. The crystalline material is practically non-elastic. Molecular-weight determinations gave negative results.

Caoutchouc purified by method (*c*), above, absorbs hydrogen in cold hexahydrotoluene solution, in presence of spongy platinum, the reaction product, after removal of the platinum, being slightly opalescent and completely stable to air, bromine, or permanganate at the ordinary temperature. On evaporation of the ethereal solution, the hydrocaoutchouc is obtained as an opaque, viscous, non-elastic, partly crystalline mass, $(C_5H_{10})_x$, which does not depress the melting point of camphor. When heated for 3 hours at 200°, then for 20 mins. at 300°, in carbon dioxide at 12 mm. pressure, no visible change takes place, but the product shows a molecular weight of 1700. The crude hydrocaoutchouc was partly distilled at 350° (bath temperature) in hydrogen at 1 mm., slight decomposition taking place only at first. The distillate, comprising one-third of the whole, had a slight odour of limonene, and was unsaturated. It was purified by solution in acetone, followed by treatment with charcoal in ether, to a colourless, saturated hydrocarbon, $C_{45}H_{92}$. The composition of the undistilled residue, which was colourless and completely saturated, corresponded with the formula $(C_5H_{10})_x$, the molecular weight (in camphor) being 1500. It had b. p. 354°/1·5 mm., the purified distillate forming a viscous, colourless mass, $C_{50}H_{102}$.

When treated with hydrogen containing 5% of oxygen, in presence of spongy platinum, purified caoutchouc afforded the unsaturated hydrocarbon, $C_{50}H_{86}$, which, however, did not react with bromine.

The bearing of the above results on the constitution is discussed, and a note on the *X*-ray examination of crystalline caoutchouc appended. F. G. W.

Ether-soluble Constituents of Lac-resin. D. N. Gupta (*J. Indian Inst. Sci.*, 1924, **7**, 142—144).—Stick-lac produced by *Lakshadia mysorensis* grown on *Shorea talura*, Roxb., was finely ground and after removal of wax with light petroleum was percolated with ether. The ethereal extract yielded myricyl alcohol, a colouring matter apparently identical with Tschirch's erythrolaccin, and giving analytical values agreeing well with tetrahydroxyanthraquinone, palmitic acid, probably myristic acid, and an unsaturated hydroxy-acid, probably $C_{15}H_{28}(OH)\cdot CO_2H$. Neither mono- nor tri-hydroxypalmitic acid was isolated. P. M.

Amygdalin. III. Synthesis of Natural *l*-Amygdalin. G. Zemplén and A. Kunz (*Ber.*, 1924, **57**, [*B*], 1357—1359).—The substance described previously (this vol., i, 975) as "stable hepta-acetyl-*l*-amygdalic acid" does not react with thionyl chloride or phosphorus pentachloride, whereas it is converted by dry methyl-alcoholic ammonia into *l*-amygdalamide which is isolated as *hepta-acetyl*-l-*amygdalamide*, m. p. 180—181°, $[\alpha]_D^{24}$ $-66\cdot3°$ in chloroform. It is hence shown to be the lactone of hexa-acetyl-*l*-amygdalic acid. The hepta-acetyl amide is converted by phosphoryl chloride into hepta-acetyl-*l*-amygdalin, $[\alpha]_D^{24}$ $-38\cdot1°$ in chloroform, which is identical with the product from natural amygdalin. The synthesis of the latter substance is rendered complete by the observation that hexa-acetyl-*l*-amygdalolactone is formed by the interaction of bromoacetogentiobiose and silver *l*-mandelate; the main product of the reaction, however, is *hepta-acetylgentiobiosidyl* l-*mandelate*, $C_6H_5\cdot CH(OH)\cdot CO\cdot C_{12}H_{14}O_{12}Ac_7$, m. p. 177°, $[\alpha]_D^{24}$ $-51\cdot76°$ in chloroform. (Cf. Campbell and Haworth, *J. Chem. Soc.*, 1924, **125**, 1337.) H. W.

***Digitalinum verum.* II.** A. Windaus, A. Bohne, and A. Schwieger (*Ber.*, 1924, **57**, [*B*], 1386—1388; cf. Windaus and Bandte, A., 1923, i, 1107; Kiliani, A., 1916, i, 493).—Analyses of digitalin, m. p. 229°, which is extracted from *Digitalinum verum* by a somewhat modified procedure, are in agreement with the formula $C_{37}H_{58}O_{14}$. The conception of the substance as a simply unsaturated trihydroxylactone in which one hydroxy group is free whilst the remaining two groups are united to dextrose and digitalose residues is confirmed by the observation that it absorbs only 1 mol. of hydrogen with formation of dihydrodigitalin. The hydrolysis of digitalin by dilute acids is accompanied by the loss of 2 mols. of water. H. W.

Saponins of *Polygala amara*. E. Glaser and H. Krauter (*Ber.*, 1924, **57**, [*B*], 1604 1610).—Two saponins are present in *Polygala amara* which can be separated from one another since one is acidic and precipitable with normal lead acetate whereas the other is neutral and is precipitated with basic lead acetate. Both are dialysable, and neither is hydrolysed by emulsin nor precipitated by ammonium sulphate. The hygroscopic, neutral saponin, $C_{34}H_{52}O_{20}$, has $[\alpha]_D$ +30° in aqueous solution. It is hydrolysed by hydrochloric acid (2%) to 3 mols. of dextrose and the *sapogenin*, $C_{14}H_{22}O_2$, m. p. 201—202°, which is optically inactive; the latter substance contains one carboxyl group, since it readily yields a *methyl* ester, $C_{15}H_{24}O_2$, m. p. 206°, which combines with bromine in chloroform solution to give the *compound* $C_{15}H_{24}O_2Br_4$, thus establishing the presence of two double bonds. Since an acid, $C_{13}H_{21}\cdot CO_2H$, with a normal carbon chain must contain three double bonds in its molecule, the presence of a ring must also be assumed. The acid saponin, $C_{22}H_{36}O_{10}$, is a brown, amorphous powder which is hydrolysed by dilute acid to equimolecular quantities of dextrose and an amorphous, acidic *sapogenin*, $C_8H_{14}O_3$, m. p. 198°, which does not react with bromine.

The reactions, solubilities, and empirical formulæ of the acid and neutral saponins render it probable that they are respectively identical with polygalasic acid and senegin derived from *Polygala senega*. H. W.

Saponin of the Primula Root. L. Kofler and H. Frauendorfer (*Arch. Pharm.*, 1924, **262**, 318—328; compare Masson, A., 1912, ii, 979).—The author has attempted to determine the nature and amount of the saponin present in radix primulæ, using the hæmolytic index of the drug as a measure of its saponin content. The drug used for the investigation was derived from *Primula veris*, and had the hæmolytic index 1 : 16,000. The saponin, prepared from the drug by extraction with 70% alcohol, precipitation with water, and purification by animal charcoal and finally by electrodialysis (compare Kofler and Dafert, this vol., ii, 74), forms a white, microcrystalline powder, m. p. 218—220°, to which is given the name primulinic acid (cf. Masson, *loc. cit.*). It is insoluble in cold water, slightly soluble in hot, and readily soluble in alkaline media, from which it is precipitated by acids. It contains C 55·04%, H 8·03%, and no nitrogen. It has a bitter taste, and induces vomiting. The hæmolytic index of the pure saponin dissolved in physiological saline, with the aid of sodium hydroxide, to neutral solution, is 1 : 190,000. Its physiological reactions are typical of a saponin. The saponin content of the drug is 8·4%, the average content of the commercial drugs being slightly greater than 5%. The solution of the above crystalline saponin in alcohol, on precipitation with ether, yields the substance in the form of a jelly, which while fresh is more soluble in water than the original form, losing this property on standing. It is therefore suggested that there are two forms of primulinic acid, a crystalline form insoluble in water, and an amorphous, soluble form, and this assumption is used to explain various solubility properties of the substance. From an alcoholic extract of the original radix primulæ, after precipitation of the saponin with ether, another substance crystallised out, which the author regards as the heptahydric alcohol volemitol, and is probably the substance which Hünefeld (*J. pr. Chem.*, 1836 and 1839) called primulin; some authors have regarded this as the saponin of the drug, although it is different from the latter in many ways. The tannin content of radix primulæ is very low. B. F.

Reduction of Sitosterol. Preparation of Dihydrositosterol or Sitostanol. R. J. Anderson and F. P. Nabenhauer (*J. Amer. Chem. Soc.*, 1924, **46**, 1953—1956).—Sitosterol having $[\alpha]$ −30·90°, prepared from wheat bran, was reduced by hydrogen in ethereal solution in the presence of platinum black. The reduction product, $C_{27}H_{47}{\cdot}OH$, colourless, hexagonal plates, m. p. 141—142°, $[\alpha]^{20}_{D}$ +24·16° in chloroform, was dihydrositosterol. It did not absorb bromine, and gave negative Liebermann–Burchard and Whitby reactions. It is very similar to, if not identical with, the saturated sterol that occurs in the endosperm of maize and wheat. That the alcoholic hydroxyl has not been changed was shown by the preparation of an *acetyl* derivative, $C_{27}H_{47}OAc$, m. p. 138—139°. A. C.

Separation of Unsaturated from Saturated Sterols. R. J. Anderson and F. P. Nabenhauer (*J. Amer. Chem. Soc.*, 1924, **46**, 1957—1960).—A mixture of sitosterol and dihydrositosterol can be almost completely separated by fractional crystallisation from alcohol, in which the latter is less soluble, if sufficient material is available. It is, however, impossible to remove the last traces of sitosterol in this way. Only the sitosterol takes up bromine, but an attempt to separate a brominated mixture of the acetyl derivatives was equally ineffective. A modification of the Liebermann–Burchard reaction (cf. A., 1885, 1075) gave satisfactory results in one operation. The mixed sterols are dissolved in carbon tetrachloride and the solution is mixed with acetic anhydride; concentrated sulphuric acid is then added while the mixture is shaken and cooled. On adding a little water and keeping the mixture, the acids form a purple upper layer containing the unsaturated sterol in solution. The saturated sterol remains dissolved in the lower carbon tetrachloride layer, partly as acetyl compound and partly as an ethereal sulphate. After distilling off the solvent, the residue is hydrolysed by means of alcoholic potassium hydroxide and yields the dihydrositosterol in a pure condition. The intensely coloured acid mixture contains the unsaturated sterol in a very stable chemical combination. On dilution with water, the colour becomes grass-green, and on neutralisation with alkali, a clear yellow. This reaction product has not been isolated in the pure form. A. C.

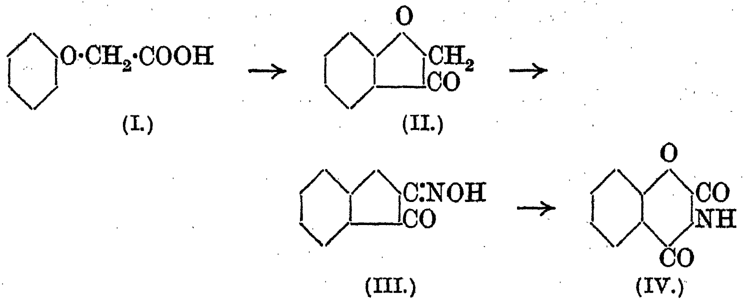
***k*-[Kombe-]Strophanthidin.** H. Thoms and F. Unger (*Z. angew. Chem.*, 1924, **37**, 721—723).—Chiefly a critical bibliographical survey (cf. Jacobs, this vol., i, 65, 67; Brauns and Closson, A., 1915, i, 435, etc.). The compound has the formula $C_{23}H_{32}O_6,\frac{1}{2}H_2O$. Its *methyl ether* has m. p. 229—230°, decomp. 232—234°. Its phenylhydrazone has a higher m. p., viz., 242—243°, than that recorded by Jacobs and Heidelberger (A., 1923, i, 123). *Dibromostrophanthidin*, $C_{23}H_{32}Br_2O_6$, has m. p. 154·5°. Other observations are briefly described. W. A. S.

Constitution of Catechin. VI. Production of Maclurin from Acacatechin. E. O. Hazleton and M. Nierenstein (*J. Amer. Chem. Soc.*, 1924, **46**, 2100—2105).—By the action of *Penicillium solitum* on a 0·72% solution of acacatechin in water containing 5% of sucrose, a yield of 86% of the theoretical amount of maclurin is produced, an observation which is not consistent with formulæ proposed for catechin by Freudenberg, Ortner, and Fikentscher (this vol., i, 660). The phenol obtained by reduction of catechin tetramethyl ether with sodium and alcohol (cf. T., 1920, **117**, 1156) which Freudenberg and Cohn (A., 1923, i, 1219) regarded as 2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxy-αγ-diphenylpropane, on ethylation with ethyl iodide gives an *ethoxy* derivative, m. p. 49—50°, which on oxidation with alkaline potassium permanganate yields *4 : 6 : 3′ : 4′-tetramethoxy-2-ethoxydiphenylacetic acid*, m. p. 137—138° (*methyl* ester, obtained by methylation of the acid with diazomethane, m. p. 64°). These results show that the fission of the chromane nucleus in acacatechin leads to the formation of an αα-diphenylpropane derivative in accordance with the structure assigned to acacatechin by Nierenstein, and not to the αγ-derivative claimed by Freudenberg and Cohn. R. B.

Oak-wood Tannin. Preparation and Purification of Tannins. I. K. Feist and H. Bestehorn (*Arch. Pharm.*, 1924, **262**, 291—304).—Oak-wood tannin is best extracted by the method of Feist and Haun (A., 1914, i, 195), with the modification that a mixture of alcohol and acetone is used for the final extraction. The crude tannin thus obtained contains about 9% of inorganic matter, notably calcium, and 5 to 30% of ellagic acid. The latter cannot be removed by crystallisation or dialysis from pyridine; a solution of the crude tannin dissolves ellagic acid to the extent of about 26% of its tannin content. The inorganic matter, but not the ellagic acid, may be completely removed by an electro-osmotic method. The purified tannin yielded a methyl derivative of molecular weight 1343. Attempts to purify the crude tannin by ultra-filtration failed. B. F.

Tetrahydrofurfuraldehyde. H. Scheibler, F. Sotscheck, and H. Friesse (*Ber.*, 1924, **57**, [*B*], 1443—1448).—Furfuraldehyde diacetate, b. p. 129°/17 mm., m. p. (plates) 52—53°, m. p. (needles) 49—51° (cf. Law, A., 1908, i, 321), is hydrogenated in ethereal solution in the presence of palladised charcoal to *tetrahydrofurfuraldehyde diacetate*, b. p. 133°/29 mm., d_4^{20} 1·1495, $n_D^{20·3}$ 1·44052. It is hydrolysed by *N*-sulphuric acid to *tetrahydrofurfuraldehyde*, a colourless, mobile liquid, b. p. 45—47°/29 mm., 142—143°/779 mm., d_4^{20} 1·0501, $n_D^{20·6}$ 1·47036; the non-crystalline *phenylhydrazone* and *oxime* and the crystalline as.-*phenylbenzylhydrazone*, m. p. 67°, are described. Furfuraldehydediethylacetal prepared by Claisen's method from furfuraldehyde and ethyl orthoformate (cf. A., 1907, i, 940) is unsuitable for the preparation of tetrahydrofurfuraldehyde since it contains unchanged aldehyde. H. W.

Transformation of Furan Rings into Oxazine Rings. E. Mameli (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 436; from *Chem. Zentr.*, 1924, i, 2517; cf. A., 1923, i, 61).—2 : 4-*Diketobenzisooxazine* (IV) has been prepared from phenol by way of the compounds I—III. The corresponding methyl derivatives have been prepared from *o*- and *p*-cresol.



G. W. R.

Formation of Coumaranones, Chromanones, and Hydroxyhydrindones from Phenols. K. von Auwers (*Annalen*, 1924, **439**, 132—175; cf. A., 1920, i, 392, 866; 1921, i, 464; 1922, i, 1192). **I. Dicyclic Ketones from *p*-Cresol and α-Bromo-α-ethylbutyric Acid** [with T. Meissner.]—*α-Bromo-α-ethylbutyryl bromide*, b. p. 94°/20 mm., reacts with *p*-tolyl methyl ether in carbon disulphide solution in presence of aluminium chloride to yield o-[*α-bromo-α-ethyl-butyryl*]-p-*cresol*, b. p. 175°/14 mm., d_4^{20} 1·307, n_{He}^{20} 1·5654. This is converted by cold sodium hydroxide into a mixture of about 2 parts of o(*α-hydroxy-α-ethylbutyryl*)-p-*cresol*, m. p. 43—44°, b. p. 166—168°/18 mm., d_4^{20} (supercooled) 1·081, n_{He}^{20} 1·5409 (*semicarbazone*, m. p. 180—181°), and 1 part of 5-*methyl*-2 : 2-*diethylcoumaranone*, b. p. 145—146°/15 mm., d_4^{20} 1·034, n_{He}^{20} 1·5326. The latter is the chief product of the reaction at 100°, and in behaving in this way the diethyl compound differs sharply from the dimethyl analogue (*loc. cit.*). When the bromobutyryl-*p*-cresol is heated with diethylaniline, 2 : 6-*dimethyl*-3-*ethylchromanone*, b. p. 151—153°, d_4^{21} 1·0627, n_{He}^{21} 1·53912 (*semicarbazone*, m. p. 210—211°; p-*nitrophenylhydrazone*, red prisms, m. p. 207—209°) is obtained; this yields a 2 : 3-*dibromo* derivative, m. p. 119—120°, and, by less prolonged treatment, a 3-*bromo* derivative, an oil, which when heated with diethylaniline gives 2 : 6-*dimethyl*-3-*ethylchromanone*, a yellow oil, b. p. 168—173°/13 mm., d_4^{20} 1·092, n_{He}^{20} 1·5540; the latter is also obtained by treating a mixture of ethyl ethylacetoacetate and *p*-cresol with phosphorus pentoxide. Only a little dimethylethylchromanone is obtained from *p*-tolyl methyl ether, α-ethylcrotonyl chloride, and aluminium chloride, the chief product being o-*butyryl*-p-*cresol*, m. p. 32—33°, b. p. 132—133°/15 mm., $d_4^{56\cdot2}$ 1·0191, $n_{He}^{56\cdot2}$ 1·5240 (p-*nitrophenylhydrazone*, red prisms,

m. p. 184—186°; with semicarbazide two *compounds*, m. p. 190° and 159—162°, respectively, were obtained). A comparison sample was prepared by treating p-*tolyl* n-*butyrate*, b. p. 140—141°, with aluminium chloride. p-*Tolyl α-bromo-α-ethylbutyrate* has b. p. 167—168° and when treated with aluminium chloride gives the above 2 : 6-dimethyl-3-ethylcoumaranone, together with 7-*hydroxy-3 : 4-dimethyl-2-ethylhydrindone*, b. p. 149·6—150·2°/8·5 mm., d_4^{20} 1·073, n_{He}^{20} 1·5484 (*semicarbazone*, m. p. 186—188°; p-*nitrophenylhydrazone*, orange-red prisms, m. p. 218—219°). p-*Tolyl α-ethylcrotonate* (from the cresol and the acid chloride) has b. p. 144—146°/12 mm., d_4^{20} 1·009, n_{He}^{20} 1·5132, and is converted by treatment with aluminium chloride at 130—140° into the above hydroxyhydrindone. Anisole and crotonyl chloride in carbon disulphide solution react with aluminium chloride to give p-*crotonylanisole*, m. p. 22°, b. p. 165—167°/15 mm., $d_4^{11\cdot7}$ 1·0906, $n_{\mathrm{He}}^{11\cdot7}$ 1·58723, the *dibromide* of which has m. p. 104·5—105·5°. 7-Hydroxyhydrindone has b. p. 128—130·5°/9·5 mm.; 7-hydroxy-2 : 4-dimethylhydrindone has b. p. 136·5—137·5°/8 mm., $d_4^{63\cdot8}$ 1·0890, $n_{\mathrm{He}}^{63\cdot8}$ 1·54501; 7-hydroxy-3 : 4-dimethylhydrindone has b. p. 140·3°/8 mm., $d_4^{63\cdot8}$ 1·0999, $n_{\mathrm{He}}^{63\cdot8}$ 1·55156. The refractivities for the α, β, and γ lines are also recorded and the relations between the optical properties and the constitutions of the above compounds are discussed.

II. Dicyclic Ketones from *m*-Cresol and α-Bromo*iso*butyric Acid [with J. Koch.]—o-(α-Bromo*iso*butyryl)*p*-cresol does not yield a coumaranone, but the corresponding derivative of *s*-*m*-xylenol readily undergoes this conversion (*loc. cit.*). It is now shown that the reaction is governed by the position of the methyl group or groups in the phenyl nucleus. Thus, when *m*-tolyl methyl ether and α-bromo*iso*butyryl bromide are treated in carbon disulphide with aluminium chloride a product is obtained from which may be separated 4(α-chloro- or α-bromo-*iso*butyryl)-*m*-cresol, 7-hydroxy-2 : 5-dimethylhydrindone, 5-hydroxy-2 : 7-dimethylhydrindone, and 2 : 2 : 4-trimethylcoumaranone; these substances were identified by comparing them with samples prepared in other ways (see below). When less aluminium chloride was used 4-(α-hydroxy*iso*butyryl)*m*-cresol also was eventually obtained. m-*Tolyl-α-bromo*iso*butyrate* (from the cresol and the acid chloride), b. p. 132—135°/11 mm., when heated at 140° with aluminium chloride yields 7-*hydroxy-2 : 5-dimethylhydrindone*, a pale yellow, steam-volatile oil, b. p. 138—139°/11 mm., d_4^{20} 1·119 or 1·123, n_{He}^{20} 1·5672 or 1·5647 (*semicarbazone*, needles, m. p. 232—233°; *phenylhydrazone*, m. p. 122—123°) and 5-*hydroxy-2 : 7-dimethylhydrindone* (not volatile in steam), m. p. 190—191°, b. p. 220°/10 mm. (*semicarbazone*, m. p. 228—229°; *acetyl* compound, m. p. 70—71°; 2 : 4 : 6-*tribromo* derivative, m. p. 169—170°). 2 : 2 : 4-*Trimethylcoumaranone* has m. p. 54—55°, b. p. 108°/10 mm., and yields the 5 : 7-*dibromo* derivative (m. p. 114°) when treated with an excess of bromine and a little aluminium. m-*Tolyl* iso*butyrate*, b. p. 104—106°/11 mm., when heated at 100° with aluminium chloride yields 4-iso*butyryl*-m-*cresol*, b. p. 120—121°/11 mm., d_4^{20} 1·042, n_{He}^{20} 1·5401, which, brominated, affords 6-*bromo*-4-(*α-bromo*iso*butyryl*)m-*cresol*, m. p. 98—99°, and 2 : 6-*di*-

bromo-4-(*α-bromoisobutyryl*)m-*cresol*, m. p. 90—92°. The latter is oxidised by hydrogen peroxide to 4 : 6-dibromo-*m*-hydroxytoluic acid. *m*-Tolyl methyl ether and α-bromopropionyl bromide yield chiefly the steam-volatile 4-(*α-chloropropionyl*)m-*cresol*, b. p. 145—147°/13 mm., which, when heated with sodium acetate and alcohol, is converted into 2 : 6-*dimethylcoumaranone*, m. p. 60—61°, b. p. 118—120°/13 mm.; the *semicarbazone*, m. p. 204—205°, was produced normally at the ordinary temperature, but at 40—50° the product was the *disemicarbazone* of 4-*pyruvyl*-m-*cresol*, which crystallises with 1 mol. H_2O and has m. p. 245°; with *p*-nitrophenylhydrazine the *dinitro-osazone* of this compound, m. p. 261°, or 275° when anhydrous, was obtained. When 2 : 6-dimethylcoumaranone is treated with sodamide and methyl iodide, 2 : 2 : 6-*trimethylcoumaranone*, m. p. 52°, b. p. 108°/12 mm. (*semicarbazone*, m. p. 250°; p-*nitrophenylhydrazone*, m. p. 196°), is obtained. When the crude steam-volatile product of the condensation of *m*-tolyl methyl ether and α-bromo*iso*butyryl bromide is shaken with cold dilute sodium hydroxide, a mixture is obtained from which may be separated 7-hydroxy-2 : 5-dimethylhydrindone, 2 : 2 : 4-trimethylcoumaranone, and 4-(*α-hydroxyisobutyryl*)m-*cresol*, m. p. 54—55° (*semicarbazone*, m. p. 154—156°; *acetyl* derivative, m. p. 56—57°, b. p. 183—185°/13 mm.); but if the oil be heated with diethylaniline a chief product is 3 : 7-*dimethylchromanone*, m. p. 55—56° (*semicarbazone*, m. p. 221°). This compound is obtained also from *m*-tolyl methyl ether and β-chloro*iso*butyryl chloride; it yields a 3-*bromo* derivative, m. p. 97—98°, which, when heated with diethylaniline, affords 3 : 7-*dimethylchromone*, m. p. 78—79°, and the latter is disrupted by boiling sodium ethoxide, giving 4-propionyl-*m*-cresol, identified as semicarbazone (see below). m-*Tolyl propionate*, b. p. 108—110°/10 mm., when treated with aluminium chloride at 100°, yields the steam-volatile 4-*propionyl*-m-*cresol*, m. p. 41·5—42·5°, b. p. 115—120°/10 mm. (*semicarbazone*, m. p. 206—208°), and 6-*propionyl*-m-*cresol*, m. p. 114—115° (*semicarbazone*, m. p. 152·5—153·5°). 2 : 6-*Dibromo*-m-*tolyl methyl ether* has m. p. 73—74°.

W. A. S.

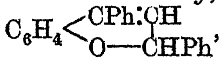
Transformation of *o*-Hydroxychalkone into Flavanone. Dehydrogenation of Flavanone to Flavone by Phosphorus Pentachloride. Synthesis of Flavone. A. LÖWENBEIN (*Ber.*, 1924, **57**, [*B*], 1515—1516).—Flavanone is readily obtained in 80% yield by the addition of excess of aqueous sodium hydroxide (1—2%) to a warm, alcoholic solution of *o*-hydroxyphenyl styryl ketone. It is converted by phosphorus pentachloride in the presence of boiling benzene into hydrogen chloride and a yellow, additive compound of flavone and phosphorus pentachloride from which the former is obtained in 80% yield by the action of alcohol.

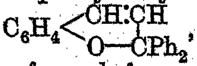
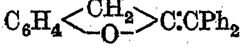
H. W.

2 : 4-Diarylchromenes. A. LÖWENBEIN [with E. PONGRÁCZ and E. A. SPIESS] (*Ber.*, 1924, **57**, [*B*], 1517—1526).—Phenyl *o*-hydroxystyryl ketone is converted by an ethereal solution of magnesium phenyl bromide into 2 : 4-*diphenylchroman-2-ol*,

$C_6H_4{<}\begin{array}{l}\mathrm{CHPh\cdot CH_2}\\ \mathrm{O{-}{-}{-}{-}CPh\cdot OH}\end{array}$, m. p. 165—166°, which is dehydrated by boiling glacial acetic acid to 2 : 4-*diphenyl*-Δ^2-*chromene*,

$$C_6H_4{<}\begin{array}{l}\mathrm{CHPh\cdot CH}\\ \mathrm{O{-}{-}{-}{-}CPh}\end{array},$$

m. p. 110°. The phenyl groups in these compounds are attached to different carbon atoms, and hence addition of the Grignard reagent to the unsaturated ketone occurs at the terminal points of the conjugated system, since phenyl *o*-hydroxystyryl ketone and magnesium *p*-tolyl bromide yield 2-*phenyl*-4-p-*tolylchroman*-2-*ol*, m. p. 141° (2-*phenyl*-4-p-*tolyl*-Δ^2-*chromene*, m. p. 85°), whereas magnesium phenyl bromide and *p*-tolyl *o*-hydroxystyryl ketone yield 4-*phenyl*-2-p-*tolylchroman*-2-*ol*, m. p. 160° (4-*phenyl*-2-p-*tolyl*-Δ^2-*chromene*, m. p. 137°). The constitution of the diphenylchromene is further confirmed indirectly, since it differs from 2 : 4-*diphenyl*-Δ^3-*chromene*,  $C_6H_4{<}\begin{array}{l}\mathrm{CPh{:}CH}\\ \mathrm{O{-}{-}CHPh}\end{array}$, m. p. 106°, obtained by dehydration of 2 : 4-*diphenylchroman*-4-*ol*, m. p. 112°; the structure of the latter compound is placed beyond doubt by its production from magnesium phenyl bromide and flavanol. The two isomeric 2 : 4-diphenylchromenes are oxidised by ferric chloride to the same 2 : 4-diphenylbenzopyrylium salts (*perchlorate*, m. p. 217—218°; *additive* compound of the chloride and ferric chloride, m. p. 168°).

Coumarin is converted by magnesium phenyl bromide in the presence of a mixture of ether and benzene into a mixture of 2 : 4-diphenylchroman-2-ol [identical with the product from phenyl *o*-styryl ketone described above and erroneously considered by Houben (A., 1904, i, 334) to be diphenyl-*o*-hydroxystyrylcarbinol] and 2 : 2-*diphenyl*-Δ^3-*chromene*,  $C_6H_4{<}\begin{array}{l}\mathrm{CH{:}CH}\\ \mathrm{O{-}{-}CPh_2}\end{array}$, m. p. 93°. The latter substance appears to be formed from coumarin without rupture of the lactone ring; it is converted by boiling glacial acetic acid or alcoholic hydrogen chloride into the *compound*, $C_6H_4{<}\begin{array}{c}\mathrm{CH}\\ \mathrm{O}\end{array}{>}C\cdot CHPh_2$ or  $C_6H_4{<}\begin{array}{c}\mathrm{CH_2}\\ \mathrm{O}\end{array}{>}C{:}CPh_2$, m. p. 239°, presumably after hydrolysis to the allene derivative,

$$OH\cdot C_6H_4\cdot CH{:}C{:}CPh_2.$$

Magnesium α-naphthyl bromide and coumarin yield 2 : 4-*di*-α-*naphthylchroman*-2-*ol*, m. p. 156°, which is converted by boiling glacial acetic acid into 2 : 4-*di*-α-*naphthyl*-Δ^2-*chromene*, m. p. 137°. The following compounds are derived from magnesium phenyl bromide and the requisite methylcoumarin: 5 : 7-*dimethyl*-2 : 4-*diphenylchroman*-2-*ol*, m. p. 111°, which yields 5 : 7-*dimethyl*-2 : 4-*diphenyl*-Δ^2-*chromene*, m. p. 118°; 4 : 6-*dimethyl*-2 : 4-*diphenylchroman*-2-*ol*, m. p. 110°, and thence 4 : 6-*dimethyl*-2 : 4-*diphenyl*-Δ^2-*chromene*, m. p. 127°; 4 : 7-*dimethyl*-2 : 4-*diphenylchroman*-2-*ol*, m. p. 144°, which yields 4 : 7-*dimethyl*-2 : 4-*diphenyl*-Δ^2-*chromene*, m. p. 86°.

[With L. Popper.]—Phenyl *o*-hydroxystyryl ketone is converted by hydrogen chloride in the presence of ether into 2-*phenylbenzo*-

pyrylium chloride, $C_{15}H_{11}OCl,HCl$, m. p. 85—86° (decomp.); the corresponding *perchlorate* has m. p. 186—187°. Either salt is converted by magnesium phenyl bromide into 2 : 4-diphenyl-Δ^2-chromene. H. W.

Preparation of Dehydracetic Acid from Ethyl Acetoacetate and the Mechanism of the Reaction. F. ARNDT and P. NACHTWEY (*Ber.*, 1924, **57**, [*B*], 1489—1491).—Dehydracetic acid is prepared in 86% yield by protracted ebullition of ethyl acetoacetate under a reflux condenser so regulated that the liberated ethyl alcohol escapes. Since dehydracetic acid is not converted by alcohol under these conditions into ethyl acetoacetate, the usual equilibrium in the decomposition of the latter depends on the action of alcohol on some intermediate product, probably the compound $COMe{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}CMe{\cdot}CH{\cdot}CO_2Et$. H. W.

Aconite Alkaloids. I. Different Isomerides of Japaconitine. R. MAJIMA, H. SUGINOMÉ, and S. MORIO (*Ber.*, 1924, **57**, [*B*], 1456—1466).—The dried tubers of various species of Japanese *Aconitum* are mixed with calcium carbonate and extracted with alcohol (95%). The alcohol is removed as completely as possible, the residue is diluted with water, extracted with light petroleum, and treated with sodium carbonate solution, whereby crude japaconitine is partly precipitated, the remainder being obtained by extraction with chloroform. The crude alkaloid is extracted with ether and the soluble portion dissolved in hydrochloric acid; the solution is fractionally precipitated with sodium carbonate. The separate fractions are converted into their hydrobromides. Japaconitines of which the hydrobromides are readily crystallised from water are termed japaconitine-*A*, whereas the suffixes -*B* and -*C* denote the alkaloids of which the hydrobromides are respectively crystallisable from a mixture of alcohol and ether or not crystallisable from this mixture or water. In various species of Japanese *Aconitum* there are found isomeric alkaloids the hydrobromides of which fall within these classes; they are designated japaconitine -A_1, -B_1, and -C_1.

The following individual substances are described, certain of which have been examined previously by Dunstan and Read (T., 1900, **77**, 45) and Makoshi (A., 1909, i, 669). The temperatures of decomposition depend greatly on the mode of heating and are determined with reference to japaconitine-*A* or its hydrobromide. The method of "mixed melting points" fails in this series. The following compounds are described: Japaconitine-*A*, $C_{34}H_{47}O_{11}N$, decomp. 202—203°, $[\alpha]_D^{18}$ +20·7° in chloroform [hydrochloride (+3·5H_2O), decomp. 160—161°; (anhydrous), decomp. 165—166°; $[\alpha]_D^{18}$ −31·3° in water; hydrobromide (+4·5H_2O), decomp. 155—156°; (anhydrous), decomp. 172—173°; hydriodide, decomp. 205—209°; chloroaurate, decomp. 159—160°; triacetyl derivative, decomp. 191—193°; *perchlorate* (+H_2O), decomp. (anhydrous), 215—218°)]. *Japaconitine*-A_1, $C_{34}H_{47}O_{11}N$, decomp. 208—209°, $[\alpha]_D^{12}$ +26·4° in chloroform [*hydrobromide* (+3·5H_2O), decomp.

(anhydrous), 172—173°, $[\alpha]_D^{16}$ $-22{\cdot}5°$ in water; *chloroaurate*, decomp. 223—224°; *perchlorate*, decomp. 215—218°]. *Japaconitine*-B, $C_{34}H_{47}O_{11}N$, decomp. 208—209°, $[\alpha]_D^{11}$ $+26{\cdot}9°$ in chloroform [*hydrochloride*, decomp. 108—109°, $[\alpha]_D^{18}$ $-24{\cdot}7°$ in water; *hydrobromide* ($+H_2O$), decomp. 179·5—180·5°, $[\alpha]_D^{30}$ $-21{\cdot}8°$ in water; *hydriodide*, decomp. 228—231°; *chloroaurate*, decomp. 235—237°; *perchlorate*, decomp. 215—218°; *triacetyl* derivative, decomp. 196—197°]. *Japaconitine*-B_1, prisms, decomp. 194—195°, $[\alpha]_D$ $+22{\cdot}0°$ in chloroform (*chloroaurate*, decomp. 248—249°). *Japaconitine*-C, $C_{34}H_{47}O_{11}N$, prisms, decomp. 195—196°, $[\alpha]_D^{12}$ $+18{\cdot}3°$ in chloroform [*chloroaurate*, decomp. 243—245°; *perchlorate* ($+2{\cdot}5H_2O$), decomp. (anhydrous), 175—178°]; *Japaconitine*-C_1, prisms, decomp. 193—195°, $[\alpha]_D$ $+23{\cdot}2°$ in chloroform (*chloroaurate*, decomp. 248—249°).

Japaconitine-*A* is hydrolysed in the presence of aqueous sulphuric acid to acetic acid and *japbenzaconine*-A, which is isolated as the hydrochloride ($+2H_2O$), decomp. 244—245°, $[\alpha]_D^{18}$ $-29{\cdot}8°$ in aqueous solution, decomp. (anhydrous) 265—266°, and by water at 160—170° to benzoic acid and japaconine-*A* (*hydrochloride*, $C_{25}H_{41}O_9N,HCl,1{\cdot}5H_2O$, decomp. 173—175°; tetra-acetyl derivative, decomp. 235—236°, $[\alpha]_D^{18}$ $-28{\cdot}9°$ in chloroform). Similarly, japaconitine-*B* yields *japbenzaconine*-B *hydrochloride*,

$$C_{34}H_{45}O_{11}N,HCl,H_2O,$$

decomp. 251—252°, $[\alpha]_D^{18}$ $-24{\cdot}4°$ in aqueous solution and japaconine-*B* which is isolated as the very hygroscopic *hydrochloride* and the *tetra-acetyl* derivative, $C_{33}H_{49}O_{13}N$, decomp. 228—229°, $[\alpha]_D^{19}$ $-19{\cdot}1°$ in alcohol. H. W.

Aconite Alkaloids. II. Aconitine and Pyraconitine. R. MAJIMA and H. SUGINOMÉ (*Ber.*, 1924, **57**, [*B*], 1466—1471).—The recognition of japaconitine as a mixture of isomerides (preceding abstract) has induced an examination of aconitine along similar lines whereby it also is found to be non-homogeneous.

Aconitine (Merck, ex *Aconito Napello*) is separated by aqueous hydrobromic acid into the readily crystallisable *aconitine*-A *hydrobromide*, decomp. 206—207°, and the amorphous *aconitine*-C *hydrobromide* (for use of suffixes, *A* and *C*, see preceding abstract). *Aconitine*-A, $C_{34}H_{47}O_{11}N$, forms hexagonal plates, decomp. 202—203°, $[\alpha]_D^{14}$ $-18{\cdot}1°$ in chloroform (*chloroaurate*, m. p. 151—152°). It is hydrolysed to *aconine*-A *hydrochloride*, $C_{25}H_{41}O_9N,HCl,2H_2O$, decomp. 169—170°, $[\alpha]_D^{9}$ $-3{\cdot}7°$ in water. *Tetra-acetylaconine*-A decomposes at 241—242°. *Aconitine*-C, $C_{34}H_{47}O_{11}N$, forms prismatic crystals, decomp. 203—204°, $[\alpha]_D^{19}$ $-23{\cdot}4°$ in chloroform (*chloroaurate*, decomp. 238—239°). It is hydrolysed to aconine-*C*, which is identified as the *tetra-acetyl* compound, decomp. 223—224°.

Thermal decomposition of japaconitine-*A* (cf. Schulze and Liebner, A., 1913, i, 1375; 1917, i, 470) yields two isomeric pyrojapaconitines designated α and β. Non-crystalline *pyrojapaconitine*-α gives a *hydrobromide*, $C_{32}H_{43}O_9N,HBr$, crystallisable from water, decomp. 262°, $[\alpha]_D^{13}$ $-43{\cdot}5°$ in water, a *perchlorate*, decomp. 252—254°, and a *chloroaurate* ($+0{\cdot}5H_2O$), decomp. 143°. *Pyrojapaco-*

nitine-β could not be caused to crystallise; it yields a *hydrobromide*, $C_{32}H_{43}O_9N,HBr,2H_2O$, decomp. 226°, $[\alpha]_D^{24}$ −68·4° in water, a *perchlorate*, decomp. 286° after darkening at 276°, and a *chloroaurate* ($+H_2O$), decomp. 176—177°. Similarly, japaconitine-*B* yields two pyrojapaconitines, one of which is identical with pyrojapaconitine-β from japaconitine-*A*. The other, termed *pyrojapaconitine*-γ, forms prismatic crystals, decomp. 169—170°, $[\alpha]_D^{26}$ −108·4° in alcohol (*hydrobromide*, $C_{32}H_{43}O_9N,HBr,2H_2O$, decomp. 240—241°, $[\alpha]_D^{25}$ −105·4° in water; *perchlorate*, decomp. 270—271°; *chloroaurate*, decomp. 202°).

Aconitine-*A* in similar manner yields two pyraconitines (α and β) in the approximate ratio 3 : 1. The α-compound resembles closely pyrojapaconitine-α, with which it is possibly identical. The following salts of pyraconitine-α are described: *hydrobromide*, $C_{32}H_{43}O_9N,HBr$, decomp. 262°, $[\alpha]_D^{15}$ −42·7° in water; *perchlorate*, decomp. 254—256°; *chloroaurate* ($+0{\cdot}5H_2O$), decomp. 143—144°. Pyraconitine-β yields a *hydrobromide*, $C_{32}H_{43}O_9N,HBr,3H_2O$, decomp. 207—208°, $[\alpha]_D^{17}$ −39·2° in water, a *perchlorate*, decomp. *ca.* 282—283°, and a *chloroaurate* ($+H_2O$), decomp. 191—192°. One of the two isomeric pyraconitines obtained from aconitine-*C* is identical with pyraconitine-β; the other, *pyraconitine*-γ, gives a non-crystalline hydrobromide and perchlorate and a *chloroaurate*, $C_{32}H_{43}O_9N,HCl,AuCl_3,H_2O$, decomp. 213—214°. H. W.

Aconite Alkaloids. III. So-called Jesaconitine. R. Majima and S. Morio (*Ber.*, 1924, **57**, [*B*], 1472—1476).—Examination of aconitum tubers grown in the region north of Tokyo discloses the presence of only two alkaloids, acetylanisoylaconine (which it is proposed to designate "jesaconitine") and japaconitine-A_2; the crude material is thus a less involved mixture than that derived from the aconitum grown in the south of Tokyo (this vol., i, 1223). The jesaconitine isolated by Makoshi (A., 1909, i, 669) from tubers grown in a similar neighbourhood and considered by him to be benzoylanisoylaconine appears to have suffered partial degradation before examination.

The extraction of the alkaloid and the separation of it into its components is effected in the manner described for japaconitine. *Jesaconitine*, decomp. 128—131°, gives a *perchlorate*,

$$C_{35}H_{49}O_{12}N,HClO_4,$$

decomp. 230—232°, $[\alpha]_D$ −16·7° in methyl-alcoholic solution, a *chloroaurate*, decomp. 208—209°, and a *perbromide*, decomp. 181—182°. When boiled with water containing the equivalent quantity of sulphuric acid, it yields jesoanisaconine (*hydrochloride*, $C_{33}H_{47}O_{11}N,HCl,3H_2O$, decomp. 209—210°, $[\alpha]_D^{20}$ −19·2° in water) and acetic acid. Hydrolysis with water at 160—170° converts it into acetic and *p*-anisic acids and jesaconine, which is found identical with aconine-*A*. Thermal decomposition of jesaconitine appears to yield a single pyrojesaconitine, which is isolated as the *perchlorate*, anhydrous prisms, decomp. 271—273°, $[\alpha]_D^{13}$ −27·4° in methyl alcohol.

Japaconitine-A_2, $C_{34}H_{47}O_{11}N$, decomp. 199—201°, $[\alpha]_D^{13}$ +18·7°

in chloroform, yields a *hydrobromide*, decomp. 172—173°, a *chloroaurate*, decomp. 143—144°, and a *perchlorate* ($+1{\cdot}5H_2O$), decomp. 214—216°, $[\alpha]_D^{13}$ $-18{\cdot}8°$ in methyl-alcoholic solution. It is hydrolysed to acetic and benzoic acids and japaconine-A_2 which is identical with aconine-A. When heated it yields pyrojapaconitine-α (hydrobromide, $C_{32}H_{43}O_9N,HBr$, decomp. 261—262°, $[\alpha]_D^{10}$ $-42{\cdot}0°$ in water; perchlorate, decomp. 250—254°; chloroaurate, decomp. 140—142°), which is probably identical with pyrojapaconitine-α and pyraconitine-α. H. W.

Mydriatic Alkaloids from the *Datura* Species. I. S. Osada (*Arch. Pharm.*, 1924, **262**, 277—291; cf. T., 1908, **93**, 2077).—The author proposes to investigate the structure of meteloidine, and reviews the literature dealing with teloidine and meteloidine, and the connexion of the former with tropine and scopoline. *Datura meteloides* is the only plant of the *Datura* species found to contain meteloidine, scopolamine and hyoscyamine being also present. The green- and violet-stalked varieties of *Datura alba*, Nees, each contained scopolamine, hyoscyamine, and atropine. Figures are given for the percentages of the different substances in various parts of the plants. B. F.

Angostura Alkaloids. I. Synthesis of Cusparine. E. Späth and O. Brunner (*Ber.*, 1924, **57**, [*B*], 1243—1251).—The synthesis of 7-methoxy-4-β-3′ : 4′-dimethoxyphenylethylquinoline and of the corresponding 2-β-3′ : 4′-dimethoxyphenylethyl compound and their non-identity with galipine disproves the constitution assigned to the latter by Troeger (A., 1913, i, 748; 1915, i, 447; 1921, i, 121). The key to the structure of cusparine and galipine is furnished by the observation that Troeger's acid, $C_{11}H_9O_3N$, is almost certainly 4-methoxyquinoline-2-carboxylic acid. Thence 4-methoxy-β-3′ : 4′-methylenedioxyphenylethylquinoline is synthesised and found identical with cusparine.

2-*Hydroxy*-7-*methoxy*-4-*methylquinoline*, m. p. 205—206° (the *hydrochloride* is described), prepared from *m*-methoxyaniline and ethyl acetoacetate, is converted successively into 2-*chloro*-7-*methoxy*-4-*methylquinoline*, m. p. 112·5—113°, and 7-*methoxy*-4-*methylquinoline*, a pale yellow liquid [*picrate*, m. p. 223·5—224° (decomp.)]. The latter substance is converted by zinc chloride and 3 : 4-dimethoxybenzaldehyde into 7-*methoxy*-4-β-3′ : 4′-*dimethoxyphenyl*-Δ^α-*ethinylquinoline hydrochloride*, which is reduced by hydrogen in the presence of palladised charcoal to 7-*methoxy*-4-β-3′ : 4′-*dimethoxyphenylethylquinoline*, m. p. 126°. 4-*Hydroxy*-7-*methoxy*-2-*methylquinoline*, m. p. 252—253° [*hydrochloride*, m. p. 269° (decomp.)], is similarly transformed successively into 4-*chloro*-7-*methoxy*-2-*methylquinoline*, m. p. 81—82°, 7-*methoxy*-2-*methylquinoline*, a liquid [*picrate*, m. p. 217° (decomp.) after softening at 204°], 7-*methoxy*-2-β-3′ : 4′-*dimethoxyphenyl*-Δ^α-*ethinylquinoline hydrochloride* and 7-*methoxy*-2-β-3′ : 4′-*dimethoxyphenylethylquinoline*, m. p. 82·5—83°.

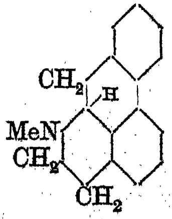
7-*Methoxyquinoline*, b. p. 143—145°/11 mm., prepared from *m*-methoxyaniline, *p*-nitrophenol, glycerol, and concentrated sulphuric acid, is converted by benzoyl chloride and potassium cyanide and hydrolysis of the nitrile into 7-*methoxyquinoline-2-carboxylic acid*, m. p. 154°. The base is converted by methyl sulphate and potassium cyanide and treatment of the product with potassium iodide into 4-*cyano*-7-*methoxyquinoline methiodide*, m. p. 204—205° (decomp.), from which 4-*cyano*-7-*methoxyquinoline*, m. p. 153—154°, is prepared in very poor yield. The nitrile is hydrolysed to 7-*methoxyquinoline*-4-*carboxylic acid*, m. p. 273° (decomp.).

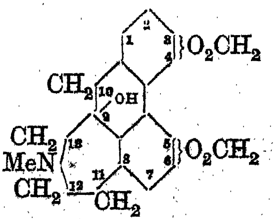
4-Methoxy-2-methylquinoline is converted by piperonal and anhydrous zinc chloride at 125° into 4-*methoxy*-2-β-3′ : 4′-*methylenedioxyphenyl*-Δ^{α}-*ethinylquinoline hydrochloride*, m. p. 193—195°, from which the corresponding *base* (dehydrocusparine), m. p. 186°, is isolated; the latter substance is reduced by hydrogen in the presence of palladised charcoal to 4-methoxy-2-β-3′ : 4′-methylenedioxyphenylethylquinoline, identical with natural cusparine.

H. W.

Chelidonium Alkaloids. III. J. Gadamer (with H. Dieterle, [Frl.] A. Stichel, M. Theyssen, and K. Winterfeld) (*Arch. Pharm.*, 1924, **262**, 249—277; cf. A., 1920, i, 75, 872; 1921, i, 579).—This paper deals with the constitution of chelidonine. *d*-Chelidonine, $C_{20}H_{19}O_5N$, with cold acetic anhydride yields *d*-*O*-acetylchelidonine, m. p. 165—166°, $[\alpha]_D$ +110°. In the hot, however, 1 mol. of water is lost, optically inactive N-*acetylanhydrochelidonine*, $C_{22}H_{19}O_5N$, m. p. 152°, being formed. The nitrogen being originally tertiary, it is clear that a ring containing it has been opened and the loss of activity indicates that an asymmetrical carbon is probably involved in the reaction. On the ground of resemblances in this and other respects with the alkaloids of the so-called aporphine group (aporphine, I, is regarded as the parent

(I.)

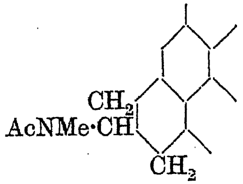


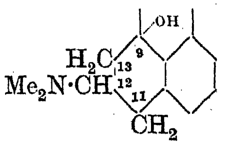


(II.)

of the phenanthrene alkaloids, and its synthesis will be reported later) a formula for chelidonine has already been suggested (A., 1920, i, 75). This is now withdrawn, and replaced by the formula II, based on the reactions cited above, together with the view that in nature the substance may be formed from phenylacetaldehyde, *N*-methyl-β-phenylethylamine, and formaldehyde, for protopine and β-homochelidonine (*allo*cryptopine), may theoretically be decomposed into these component parts. The suggested formation in nature of chelidonine from these components is outlined. The formation of *N*-acetylanhydrochelidonine may be explained by fission of the ring between the nitrogen and C_{13}, re-closing of the ring between C_{13} and C_{12}, and loss of water between C_{10} and the asymmetric atom C_9, giving (III).

(III.)





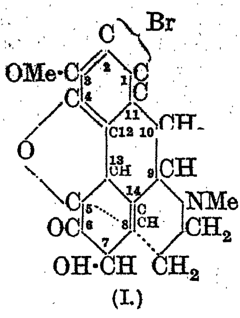
(IV.)

[With H. Dieterle.]—When treated with methyl iodide, chelidonine first affords *chelidoninemethine*-A, $C_{21}H_{21}O_5N$, m. p. 145—146°, $[\alpha]_D$ $-271\cdot3°$ in chloroform (also formed by the action of methyl iodide on *O*-acetylchelidonine), and *chelidoninemethine*-B, m. p. 107—108°, $[\alpha]_D$ $-100°$, which occurs in the mother-liquor of the *A* methine as prepared by the first method. These two are regarded as stereoisomerides, and it is concluded that their formation is due to fission of the 7-ring and its reclosing, as in the case of the acetylation, so that the bases have formula IV. The existence of two stereoisomerides is due to the fact that a new asymmetric atom (12) has been superimposed on the original one (9). On further treatment with methyl iodide the *A* methine yields the corresponding *chelidoninemethinium methiodide*, $C_{22}H_{24}O_5NI$, m. p. 232—234° (decomp.), $[\alpha]_D$ $-50°$, which rapidly racemises in solution. The action of hot acetic anhydride on the *A* methine or its methiodide furnishes an optically inactive *substance*, $C_{21}H_{18}O_6$, m. p. 157—159° (the by-products being dimethylacetamide and trimethylamine respectively). The latter substance is an acetyl derivative, for on deacetylation by Schiff's method it yields a *substance*, $C_{19}H_{16}O_5$, m. p. 170—171°, resistant to oxidation. By the action of methyl sulphate on *O*-acetylchelidonine or chelidonine and subsequent treatment with sodium hydroxide there is formed optically inactive *methylanhydrochelidonine*, $C_{21}H_{19}O_4N$, m. p. 152—153°, probably by loss of water between C_9 and C_{10}; the same substance is formed by the action of methyl iodide on chelidonine under special conditions. Methylanhydrochelidonine forms a *methiodide*, $C_{22}H_{22}O_4NI$, m. p. 242—244°, which may be readily converted into the corresponding *methonitrate*, $C_{22}H_{22}O_6N_2$, m. p. 260—261°, and *methochloride*, m. p. 215—217°. On reduction with sodium amalgam, the latter yields trimethylamine and the *substance*, $C_{19}H_{14}O_4$, m. p. 244—245°, which is resistant towards permanganate, and is regarded as containing a phenanthrene nucleus. Methylanhydrochelidonine methiodide, on treatment with moist silver oxide, probably gives rise to the corresponding *hydroxide*; the latter, however, was not isolated, but immediately distilled under reduced pressure, when trimethylamine was evolved. *ψ-Anhydrochelidonine*, $C_{20}H_{17}O_4N$, m. p. 89—89·5°, was prepared from its *hydrochloride*, m. p. 204—205°, which results from the hydrolysis of *N*-acetylanhydrochelidonine with hydrochloric acid. Methyl iodide converts ψ-anhydrochelidonine into methylanhydrochelidonine methiodide, a *substance*, m. p. 133—134°, being formed as a by-product. In both methods of preparation of the *A* methine there is formed as a by-product a *tertiary base*, m. p. 195—198°, $[\alpha]_D$ +83° (in 2% chloroform solution). As a by-product in the treatment of chelidonine with methyl sulphate, there is formed O-*methylchelidonine*, $C_{21}H_{21}O_5N$, m. p. 162—163°, $[\alpha]_D$ +186° (in 0·5% alcohol solution), converted on heating with acetic anhydride into *N*-acetylanhydrochelidonine.

For purposes of simplicity, the breaking of the 7-ring has been consistently regarded as occurring between the nitrogen and C_{13}; actually it may also occur between N and C_{12}, which would result in the possibility of a new set of formulæ. B. F.

Action of Reducing Agents on Bromocodeinone. E. SPEYER and K. SARRE (*Ber.*, 1924, **57**, [*B*], 1404—1409).—Bromocodeinone, prepared by a modification of Freund's method (A., 1906, i, 303), is reduced by hydrogen in acetic acid solution in the presence of palladised charcoal to dihydrocodeinone, identical with the product described by Freund and Speyer (A., 1921, i, 126) and by Mannich and Löwenheim (A., 1921, i, 125). When electrolytically reduced in sulphuric acid solution (25%) at lead electrodes, bromocodeinone yields *dihydrodeoxycodeine*, $2C_{18}H_{23}O_2N,EtOH$, decomp. 139—140°, $[\alpha]_D^{13}$ +58·15° in dilute acetic acid solution, the product being formed by the replacement of bromine by hydrogen, reduction of the 6-keto to the methylene group, and rupture of the oxygen bridge with formation of a hydroxy group. It yields a *salicylate*, m. p. 198°, a *methiodide*, m. p. 199°, and a methyl ether which is isolated as the *methiodide*, m. p. 245°. Concentrated potassium hydroxide solution transforms the latter substance into the non-crystalline demethyldihydrodeoxycodeine methyl ether (*hydriodide*, $C_{20}H_{27}O_2N,HI$, m. p. 220° after softening; *methiodide*, m. p. 103°). The latter substance loses trimethylamine when heated with potassium hydroxide, but the nitrogen-free product was too unstable to be isolated. Reduction of dihydrodeoxycodeine in the presence of colloidal palladium gives β-tetrahydrodeoxycodeine (cf. Freund, A., 1920, i, 759). H. W.

Action of Bromine on Hydroxycodeinone and Hydroxydihydrocodeinone. E. SPEYER and K. SARRE (*Ber.*, 1924, **57**, [*B*], 1409—1422).—Hydroxycodeinone hydrobromide (cf. Freund and Speyer, A., 1917, i, 217) dissolved in cold water is converted by bromine water into *bromohydroxycodeinone* (I), m. p. 204—205°, $[\alpha]_D^{13}$ −80·21° in acetic acid solution; the corresponding *hydrobromide*, decomp. 280° after softening, *acetyl* derivative, m. p. 238°, and *phenylhydrazone*, decomp. 250°, are described. The substance is converted by hydrogen in the presence of palladium into hydroxydihydrocodeine, m. p. 218—220°. If, however, hydroxycodeinone is brominated in boiling glacial acetic acid solution, a perbromide is produced which is transformed by alcohol into *dibromohydroxycodeinone*, m. p. 194—195°, $[\alpha]_D^{13}$ −120·4° in



(I.)

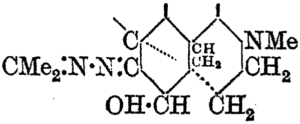
acetic acid solution; this substance gives a *hydrobromide*, decomp. 265°, an *acetyl* derivative, m. p. 219°, and a *phenylhydrazone*, decomp. 238°. It resists dehalogenation by the usual methods, but is converted by catalytic hydrogenation into hydroxydihydrocodeinone, m. p. 218—220°. Since it is also produced by the bromination of bromohydroxycodeinone in boiling glacial acetic acid, the primary action is considered to consist of addition of bromine at positions 8 and 14 (see I) followed by loss of hydrogen bromide, leaving the second bromine atom in position 8. Confirmation of this hypothesis is found in the observation that dibromohydroxycodeinone is converted by sodium hyposulphite [which has been observed previously (Freund and Speyer, *loc. cit.*) to effect saturation of the double bond between the carbon atoms 8 and 14] into *bromohydroxydihydrocodeinone*, m. p. 182° (*hydrobromide*, decomp. 227—230° after softening, $[\alpha]_D^{18}$ $-93{\cdot}15°$ in aqueous solution; *monoacetyl* derivative, m. p. 217°; *semicarbazone*, decomp. 249°). Bromohydroxydihydrocodeinone is also obtained by the action of bromine water on a cold, aqueous solution of hydroxydihydrocodeinone hydrobromide and by the action of sodium hyposulphite on bromohydroxycodeinone; it is converted by palladium and hydrogen into hydroxydihydrocodeinone.

The action of bromine on hydroxydihydrocodeinone dissolved in boiling glacial acetic acid yields a crystalline *perbromide* from which *tribromohydroxydihydrocodeinone*, $C_{18}H_{18}O_4NBr_3$, decomp. 228° after softening, $[\alpha]_D^{18}$ $-225{\cdot}56°$ in acetic acid solution, is prepared. The compound is also obtained by the bromination under similar conditions of bromohydroxydihydrocodeinone, into which it is reconverted by sodium hyposulphite. The bromine atoms are hence considered to occupy the positions 1 or 2, 8 and 14 (see I). It gives a *hydrobromide*, decomp. 255°, and an *acetyl* derivative, decomp. 220° after softening. The tribromo compound is converted by 2*N*-sodium hydroxide solution into a feebly basic *substance*, $C_{18}H_{20}O_6NBr,H_2O$, decomp. 302° after softening, which is regarded as bromo-7 : 8 : 14-trihydroxydihydrocodeinone; it yields, however, only a *monoacetate* ($+H_2O$), decomp. 267°. Dehalogenation by means of hydrogen and palladium yields 7 : 8 : 14-*trihydroxydihydrocodeinone*, decomp. 320° after softening, $[\alpha]_D^{18}$ $-76{\cdot}55°$ in feebly alkaline solution.

Hydroxycodeinone-*N*-oxide (cf. Freund and Speyer, *loc. cit.*) which has now been obtained in the crystalline form, decomp. 243°, is converted by acetic anhydride and sulphuric acid into "*ordinary*" *hydroxycodeinone*-N-*oxidesulphonic acid*, long rodlets, decomp. above 260°, and *α-hydroxycodeinone*-N-*oxidesulphonic acid*, rectangular leaflets, incipient decomp. 270°. The former acid is converted by sulphurous acid into *hydroxycodeinonesulphonic acid*, decomp. 310°. Attempts to replace the sulphonic group by bromine were unsuccessful.

H. W.

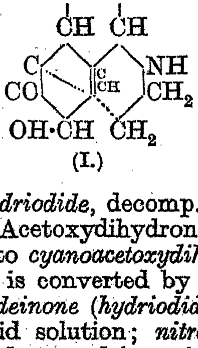
Catalytic Hydrogenation of Hydroxycodeinone- and Hydroxydihydrocodeinone-hydrazones by Palladium and Hydrogen. E. SPEYER and K. SARRE (*Ber.*, 1924, 57, [*B*], 1422—[illegible]).—Hydroxycodeinone is readily converted by hydrazine hydrate into the corresponding *hydrazone*, m. p. 221—222°, which does not appear to yield the desired methylene derivative when heated with sodium ethoxide solution under pressure. Hydroxydihydrocodeinone and hydrazine hydrate in the presence of glacial acetic acid give *hydroxydihydrocodeinonehydrazone*, $C_{18}H_{23}O_3N_3$, m. p. 213—214° (slight decomp.); it is not reduced by hydrogen and palladium in dilute acetic acid solution. Under similar conditions, hydroxycodeinonehydrazone absorbs 2 mols. of hydrogen with production of ammonia and *hydroxydihydrocodeinoneketimine*, $C_{18}H_{22}O_3N_2$, m. p. 216—217° after softening, which is readily hydrolysed by acids to ammonia and hydroxydihydrocodeinone. If hydrogenation is effected in the presence of aqueous acetone, only 1 mol. of hydrogen is absorbed and *hydroxydihydrocodeinonedimethylketazine* (I), m. p. 159°, is produced. Hydroxycodeinonehydrazone condenses with acetone in the presence of ammonia to give *hydroxycodeinonedimethylketazine*, m. p. 171°, which could not be hydrogenated satisfactorily to the dihydro compound described above.



(I.)

H. W.

Action of Cyanogen Bromide on Hydroxycodeinone and Hydroxydihydrocodeinone. E. Speyer and K. Sarre (*Ber.*, 1924, 57, [*B*], 1427—1430).—Hydroxycyanonorcodeinone (Freund and Speyer, A., 1917, i, 217) is converted by boiling sulphuric acid (25%) into *hydroxynorcodeinone* (cf. I), decomp. 218°, $[\alpha]^{18}_{D}$ —123·33° in dilute acetic acid solution. It yields a crystalline *hydrobromide* and a *nitroso* derivative, m. p. 234°. It is converted by sodium ethoxide and allyl bromide into the non-crystalline *allylnorhydroxycodeinone*, characterised as the *hydriodide*, decomp. 192°.



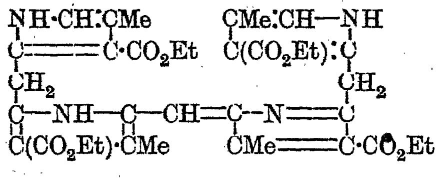
(I.)

Acetoxydihydronorcodeinone is converted by cyanogen bromide into *cyanoacetoxydihydronorcodeinone*, decomp. 256° after softening. It is converted by sulphuric acid into the oily *hydroxydihydronorcodeinone* (*hydriodide*, decomp. 295°, $[\alpha]^{18}_{D}$ —114·54° in dilute acetic acid solution; *nitroso* derivative, decomp. 259°). *Allylhydroxydihydronorcodeinone* is a liquid which gives a crystalline *hydrobromide*, decomp. 182°. The pharmacological action of the allyl derivatives is opposite to that of the parent compounds, as is to be expected when the methyl is replaced by the allyl group (cf. von Braun, A., 1917, i, 163).

H. W.

Strychnos Alkaloids. XLIII. Decomposition of the Azide of Dihydrobrucinonic Acid. H. Leuchs and S. Kanao (*Ber.*, 1924, 57, [*B*], 1318—1320; cf. A., 1923, i, 942).—Ethyl dihydrobrucinonate is converted successively into the corresponding *hydrazide*, decomp. 205° after softening at 185°, and azide. The latter is decomposed by boiling water into azoimide, formaldehyde, and an iso*brucinolone hydrate*, $C_{21}H_{24}O_6N_2$, m. p. 295° (decomp.) after darkening at 260°, $[\alpha]^{20}_{D}$ +89·4° in glacial acetic acid solution (*acetyl* derivative, m. p. 210—212°, $[\alpha]^{20}_{D}$ +94·8° in glacial acetic acid). The *iso*brucinolone hydrate is not identical with that obtained from *iso*brucinolone and hydrochloric acid (Leuchs and Brewster, A., 1912, i, 210). H. W.

Action of Halogens on Substituted Pyrroles. Synthesis of a Dipyrrylethane and of a Colouring Matter with Four Pyrrole Nuclei in its Molecule. H. FISCHER and H. SCHEYER (*Annalen*, 1924, **439**, 185—195; cf. this vol., i, 80).—Aniline interacts with ethyl 4-methyl-2-bromomethylpyrrole-3 : 5-dicarboxylate (A) to give *ethyl* 4-*methyl*-2-*anilinomethylpyrrole*-3 : 5-*dicarboxylate*, m. p. 125—126°, and with ethyl 3-bromo-4-methyl-2-bromomethylpyrrole-5-carboxylate (B) to give *ethyl* 3-*bromo*-4-*methyl*-2-*anilinomethylpyrrole*-5-*carboxylate*, m. p. 128—129°. (A) also reacts with phenylhydrazine, forming α-(4-*methyl*-3 : 5-*dicarbethoxy*-2-*pyrrylmethyl*)α-*phenylhydrazine*, m. p. 120—121°, the asymmetric structure of which is demonstrated by the fact that with benzaldehyde it affords a *hydrazone*, rhombs, m. p. 116—117°. (B) gives a similar product, namely, α-(3-*bromo*-4-*methyl*-5-*carbethoxy*-2-*pyrrylmethyl*)α-*phenylhydrazine*, m. p. 126°. With hydrazine itself, (A) yields αα-di-(4-*methyl*-3 : 5-*dicarbethoxy*-2-*pyrrylmethyl*)*hydrazine*, m. p. 130—131°, which affords with benzaldehyde a *hydrazone*, m. p. 129—130°, and with ethyl 2 : 4-dimethylpyrrole-3-aldehyde-5-carboxylate also a *hydrazone*, m. p. 162—163° after softening; when the hydrazine is treated with cuprammonium acetate solution, nitrogen is evolved, and *s*-*di*-(4-*methyl*-3 : 5-*dicarbethoxy*-2-*pyrryl*)*ethane*, needles, m. p. 161°, is produced. The latter suffers hydrolysis to the *dicarboxylic acid* (the *sodium* salt is described) when treated with sodium hydroxide solution, only the two 5-carbethoxy groups being affected; when the sodium salt of this is treated with formic and hydrochloric acids the carboxyl groups are displaced and 5 : 5′-*di*-(4″-*methyl*-3″-*carbethoxy*-β-*pyrrylethyl*-)3 : 3′-*dimethyl*-4 : 4′-*dicarbethoxy*-2 : 2′-*dipyrrylmethene* (annexed formula), m. p. 277° (decomp.), is produced. This is an intensely yellow-coloured substance, closely resembling mesobilirubin in colour.

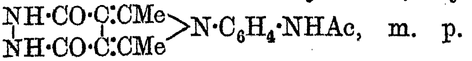
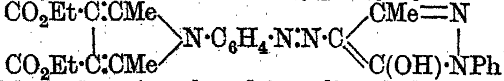


Ethyl 2 : 4-dimethylpyrrole-5-carboxylate is converted by treatment with bromine (2 mols.) into (B), which was previously obtained (*loc. cit.*) by another method. When 3-acetyl-2 : 4-dimethylpyrrole is treated with iodine 5-*iodo*-3-*acetyl*-2 : 4-*dimethylpyrrole*, m. p. 160° (decomp.), is obtained. The iodine atom here is not very mobile, but when the compound is treated with bromine the same methene is produced as is afforded when the unsubstituted pyrrole is treated with an excess of bromine (*loc. cit.*). *Ethyl* 5-*iodo*-2 : 4-*dimethylpyrrole*-3-*carboxylate*, m. p. 146°, *ethyl* 3-*iodo*-

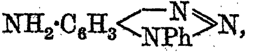
2 : 4-*dimethylpyrrole-5-carboxylate*, m. p. 141°, and *ethyl 4-iodo-2 : 5-dimethylpyrrole-3-carboxylate*, m. p. 136°, are also described.
W. A. S.

Synthesis of Phyllopyrrolecarboxylic Acid (Synthesis of the Acid Scission Products of Blood Pigment. II). H. Fischer and C. Nenitzescu (*Annalen*, 1924, **439**, 172—184; cf. this vol., i, 543).—2 : 4 : 5-Trimethylpyrrole-3-aldehyde reacts with malonic acid in presence of piperidine (the aldehyde forms an *additive* compound with piperidine, m. p. 145°) to yield 2 : 4 : 5-*trimethylpyrrole*-3(β)-*acrylic acid*, a green, not very stable substance, m. p. 203°, which is readily reduced by sodium amalgam to 2 : 4 : 5-trimethylpyrrole-3(β)-propionic acid, m. p. 88° (picrate, m. p. 124°) identical with phyllopyrrolecarboxylic acid obtained from hæmin. When the above aldehyde is condensed with malononitrile, 2 : 4 : 5-*trimethyl*-3-(*ωω-dicyanovinyl*)*pyrrole*, greenish-yellow needles, m. p. 185°, is obtained. This substance resists hydrolysis; by the action of sodium hydroxide, the aldehyde is regenerated, and sulphuric acid causes profound decomposition. By a similar condensation, using cyanoacetic acid, 2 : 4 : 5-*trimethyl*-3-(*ω-cyano-ω-carboxyvinyl*)*pyrrole*, green crystals, m. p. 214°, was prepared. This also cannot be hydrolysed, but when heated at its m. p. decomposes, giving 2 : 4 : 5-*trimethyl*-3-(*ω-cyanovinyl*)*pyrrole*, olive-green needles, m. p. 154°, which, when treated with sodium amalgam, undergoes reduction and hydrolysis, giving phyllopyrrolecarboxylic acid, identical with that previously obtained. 2 : 5-Dimethyl-4-carbethoxypyrrole-3-aldehyde also reacts with malonic acid to afford directly 2 : 5-*dimethyl*-4-*carbethoxypyrrole*-3(β)-*acrylic acid*, yellow scales, m. p. 230° (decomp.), which, when reduced with sodium amalgam, yields 2 : 5-*dimethyl*-4-*carbethoxypyrrole*-3(β)-*propionic acid*, m. p. 178°. The latter may also be obtained synthetically by heating with ammonium acetate at 160° the oily ethyl αβ-diacetyladipate formed by interaction of ethyl acetylbromobutyrate and ethyl sodioacetoacetate; the ester obtained is readily hydrolysed by warm potassium hydroxide. When the dimethylcarbethoxypyrrolepropionic acid of either provenance is heated at 220° with potassium methoxide and methyl alcohol, it yields phyllopyrrolecarboxylic acid. W. A. S.

Condensations of Acetyl-*p*-phenylenediamine to Derivatives of Pyrrole and their Hydrolytic Fission. C. Bülow and W. Dick (*Ber.*, 1924, **57**, [*B*], 1281—1285).—Ethyl diacetylsuccinate reacts with acetyl-*p*-phenylenediamine in boiling glacial acetic acid solution to yield *ethyl* 1-p-*acetamidophenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*, m. p. 198—199°, which is hydrolysed by alcoholic potassium hydroxide solution to 1-p-*acetamidophenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylic acid*, m. p. 252° (decomp.) [the *potassium* salt and the *hydrochloride* are described]. The acid is transformed at 250—255° into 1-p-*acetamidophenyl*-2 : 5-*dimethylpyrrole*, m. p. 192°, which is also obtained directly from acetonylacetone and acetyl-*p*-phenylenediamine. The ester is very slowly hydrolysed to the corresponding acid by aqueous alkali hydroxides,

but readily suffers fission of the pyrrole ring into its components under the influence of acids. With hydrazine, it yields the cyclic *hydrazide*, 
$$\left.\begin{array}{l}NH\cdot CO\cdot C{:}CMe\\ NH\cdot CO\cdot C{:}CMe\end{array}\right>N\cdot C_6H_4\cdot NHAc$$
m. p. above 300°. Ethyl diacetylsuccinate and *p*-nitroaniline yield *ethyl* 1-p-*nitrophenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*, m. p. 94°, which is reduced by zinc dust and hydrochloric acid to *ethyl* 1-p-*aminophenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*, m. p. 117°. The diazotised ester is coupled with the requisite component to yield *ethyl* 1-p-*aminophenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylateazo*-β-*naphthol*, m. p. 166°, *ethyl* 1-p-*aminophenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylateazoacetoacetanilide*, m. p. 155°, and the corresponding p-*phenetidide*, m. p. 178°. The latter compounds are converted by phenylhydrazine into the *substance* 
$$\left.\begin{array}{l}CO_2Et\cdot C{:}CMe\\ CO_2Et\cdot C{:}CMe\end{array}\right>N\cdot C_6H_4\cdot N{:}N\cdot C\left<\begin{array}{l}CMe{=}N\\ C(OH)\cdot NPh\end{array}\right.$$
m. p. 154—156°. Ethyl 1-*p*-nitrophenyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate and ethyl 1-phenyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate suffer fission of the pyrrole ring under the influence of mineral acids; this reaction appears therefore to be general.

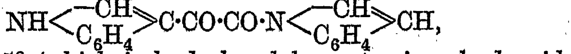
H. W.

Synthesis of 1-Aminocarbazole. H. LINDEMANN and F. WERTHER (*Ber.*, 1924, 57, [*B*], 1316—1318).—7-Nitro-1-phenylbenzotriazole is reduced by stannous chloride and hydrochloric acid to 7-*amino*-1-*phenylbenzotriazole*, 
$NH_2\cdot C_6H_3\left<\begin{array}{c}N\\ NPh\end{array}\right>N$, m. p. 163° (*acetyl* derivative, m. p. 166°), which, when heated at 300° in paraffin, yields 1-*aminocarbazole*, m. p. 193° (*diacetyl* compound, m. p. 186°). Since the amine is also produced by the action of sodium hyposulphite on an alkaline-alcoholic solution of the nitrocarbazole, m. p. 187°, isolated by Lindemann as by-product of the nitration of nitrosocarbazole (this vol., i, 550), the latter must be 1-nitrocarbazole; the compound described thus in the literature is therefore the 2- or 4-nitro derivative. H. W.

Carbazole Derivatives. I. R. SEKA (*Ber.*, 1924, 57, [*B*], 1527—1530).—Ethyl carbazole-9-acetate is converted by alcoholic ammonia at 120° into *carbazole*-9-*acetamide*, $C_{12}H_8N\cdot CH_2\cdot CO\cdot NH_2$, m. p. 244°, and by hydrazine hydrate at 125° into *carbazole*-9-*acethydrazide*, m. p. 258—258·5° (*benzylidene* derivative, m. p. 267·5°; *hydrochloride*, m. p. above 320°). The hydrazide is converted through the azide into the corresponding *urethane*, $C_{12}H_8N\cdot CH_2\cdot NH\cdot CO_2Et$, m. p. 133·5°. *Diphenyl*-9-*carbazolylmethylcarbinol*, $C_{12}H_8N\cdot CH_2\cdot CPh_2\cdot OH$, m. p. 147°, is prepared by the action of an excess of magnesium phenyl bromide on ethyl carbazole-9-acetate. H. W.

Synthesis in the Indole Group. III. Formation of N-Acylindoles. R. MAJIMA and T. SHIGEMATSU (*Ber.*, 1924, 57, [*B*], 1449—1453).—The addition of ethyl acetate to a solution of magnesium indolyl iodide in ether or anisole leads to the formation of

1-acetylindole; the solvent does not play the same decisive part as in the action of magnesium indolyl iodide and formic ester (Majima and Kotake, A., 1923, i, 150). Magnesium indolyl iodide and ethyl oxalate yield a mixture 1 : 1′-*oxalyldi-indole*, $C_{18}H_{12}O_2N_2$, m. p. 154·5—156°, 3-*indolylglyoxylyl*-1-*indole*,



$$NH{<}\genfrac{}{}{0pt}{}{-CH}{C_6H_4}{>}C\cdot CO\cdot CO\cdot N{<}\genfrac{}{}{0pt}{}{-CH}{C_6H_4}{>}CH,$$

m. p. 224—225° (which is hydrolysed by potassium hydroxide to indole, and *indolyl-3-glyoxylic acid*, decomp. 215° after darkening at 186°), and *ethyl indolyl-3-glyoxylate*, m. p. 185—186°. The compound designated 1 : 1-di-indolyl prepared by Oddo and Sanna (A., 1922, i, 371) by the action of oxalyl chloride on magnesium indolyl bromide is 3-indolylglyoxylyl-1-indole.

[With T. Rokkaku.]—Ethyl malonate does not appear to react with magnesium indolyl iodide in the presence of anisole.

[With T. Ikeda.]—Ethyl succinate and magnesium indolyl iodide yield *succinyl*-1 : 1′-*di-indole*, $C_{20}H_{16}O_2N_2$, m. p. 217—218°.

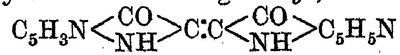
H. W.

Syntheses in the Indole Group. IV. Indolylketonic Acids. R. Majima, T. Shigematsu, and T. Rokkaku (*Ber.*, 1924, **57**, [*B*], 1453—1456).—The action of carbomethoxyformyl chloride on an ethereal solution of magnesium indolyl iodide gives a little 3-indolylglyoxylyl-1-indole (cf. preceding abstract) and, mainly, *methyl* 3-*indolylglyoxylate*, m. p. 220—222° (*phenylhydrazone*, m. p. 133—136°). The *oxime*, m. p. 149—151°, and the *oxime* of the corresponding ethyl ester, m. p. 138—142°, are prepared by means of hydroxylamine hydrochloride and potassium acetate in alcoholic solution. If, however, the ester is warmed with the equivalent quantity of free hydroxylamine, 3-*indolylglyoxylic acid oxime*, decomp. about 151°, is produced. *Ethyl* 3-*indolylacetate*, $C_8H_6N\cdot CO\cdot CH_2\cdot CO_2Et$, m. p. 119·5°, prepared from magnesium indolyl iodide and carbethoxyacetyl chloride, is readily transformed by alcoholic potassium hydroxide solution into methyl 3-indolyl ketone. The ester is converted by phenylhydrazine into 1-*phenyl*-3-β-*indolylpyrazolone*, $C_{17}H_{13}ON_3$, m. p. 201—203°, and by hydroxylamine into 3-β-*indolyl*isooxazolone, $C_{11}H_8O_2N_2$, m. p. 188—188·5°.

[With T. Ikeda.]—*Ethyl* β-3-*indolylpropionate*, prepared from magnesium indolyl iodide and β-carbethoxypropionyl chloride, has m. p. 129·5—130·5°; the corresponding *acid*, m. p. 235—236°, is described. The ester is decomposed by molten potassium hydroxide with production of indole-3-carboxylic acid in small amount.

[With I. Miyagawa.]—Cyanogen chloride and magnesium indolyl iodide yield 3-*cyanoindole*, m. p. 178—180·5°. 3-*Cyano*-2-*methylindole*, m. p. 210—212°, is unusually resistant to hydrolysis by alkali hydroxide. H. W.

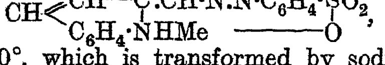
New Class of Indigoid Dyes. F. Reindel (*Ber.*, 1924, **57**, [*B*], 1381—1386).—2-Aminopyridine is converted by chloroacetic acid into *pyridylglycine*, $C_7H_8O_2N_2$, m. p. 250° (decomp.), which is transformed by boiling sodium hydroxide solution into the *sodium* salt of *pyrindoxyl*, $C_5H_3N<\genfrac{}{}{0pt}{}{C(ONa)}{NH\text{——}}>CH$ or $NH{:}C_5H_3\leqslant\genfrac{}{}{0pt}{}{C(ONa)}{N\text{———}}\geqslant CH$. The constitution of the salt is thus far established by its ability to give a *monobenzoyl* derivative, m. p. 293° (decomp.) after softening at 275°, which is soluble in alkali hydroxide solution, and an insoluble *dibenzoyl* compound, m. p. 172—173°, when benzoylated according to the Schotten–Baumann reaction, whereas when treated with benzoyl chloride in the presence of pyridine it yields a *benzoyl* derivative, m. p. 130°, which is insoluble in alkali hydroxide. The *barium, copper, lead, cobalt,* and *nickel* salts of pyrindoxyl have been examined; the *hydrochloride*, $C_7H_7ON_2Cl$, m. p. 243° (decomp.) after darkening at 230°, and the *picrate*, decomp. 207—208°, are described. The sodium salt is oxidised by an aqueous solution of potassium ferricyanide to the indigoid *dye*,



$$C_5H_3N<\genfrac{}{}{0pt}{}{CO}{NH}>C{:}C<\genfrac{}{}{0pt}{}{CO}{NH}>C_5H_5N$$

or $C_5H_3(NH)\leqslant\genfrac{}{}{0pt}{}{CO}{N\text{—}}>C{:}C<\genfrac{}{}{0pt}{}{CO}{\text{—}N}\geqslant C_5H_3NH$, a red amorphous powder which is readily reduced beyond the indigo-white stage by sodium hyposulphite, but yields a typical vat with zinc dust and sodium hydroxide. On cotton mordanted with tannin and tartar emetic, it gives raspberry-red shades which are fast to light but not to milling. H. W.

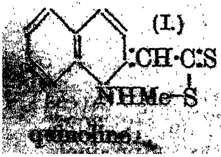
Reactions of 2-Methylene-1-alkyl-1 : 2-dihydroquinolines. I. Diazo Coupling of the Methylene Base in Neutral Solution. E. Rosenhauer [with O. Dannhofer] (*Ber.*, 1924, **57**, [*B*], 1291—1294).—2-Methylene-1-methyl-1 : 2-dihydroquinoline dissolved in ether couples with a neutral, aqueous solution of benzenediazonium chloride without loss of the *N*-methyl group (contrast König, A., 1923, i, 862) to form 2-*benzeneazomethylene*-1-*methyl*-1 : 2-*dihydroquinoline hydrochloride*, decomp. 243°, from which the free base, m. p. 140—141°, is obtained; the latter compound is identical with that prepared from 2-bromomethylquinoline methobromide and phenylhydrazine (Rosenhauer, this vol., i, 768). When cautiously oxidised with potassium permanganate, it yields 1-methyl-2-quinolone. Similarly, the methylene base and diazobenzenesulphonic acid give the "internal" *p*-*sulphonate* of 2-*benzeneazomethylene*-1-*methyl*-1 : 2-*dihydroquinoline*,



$$CH\leqslant\genfrac{}{}{0pt}{}{CH\text{—}C{:}CH{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SO_2}{C_6H_4{\cdot}NHMe\text{ ——————— }O},$$

decomp. above 300°, which is transformed by sodium hydroxide into the *sodium* salt of 2-*p*-sulphobenzeneazomethylene-1-methyl-1 : 2-dihydroquinoline.

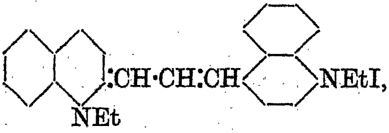
[With A. Schmidt and W. Schleifenbaum.]—2-Methylene-1-methyl-1 : 2-dihydroquinoline dissolved in benzene is converted by a large excess of carbon disulphide into the compound I, decomp. 185°. A similar *substance*, $C_{13}H_{13}NS_2$, decomp. 185°, is derived from 2-methylene-1-ethyl-1 : 2-dihydroquinoline. H. W.



(I.)

Degradation of Pyridine to Glutacondialdehyde and Reconversion of the Latter into Pyridine. I. P. BAUMGARTEN.—(See i, 1166.)

Cyanine Dyes. VIII. Synthesis of a 2 : 4′-Carbocyanine. Constitution of the Dicyanines. W. H. MILLS and R. C. ODAMS (*J. Chem. Soc.*, 1924, **125**, 1913—1921).—When a mixture of 4-methyl- and 2-methyl-quinoline ethonitrates is heated in pyridine solution with diformylmethylaminodiphenyl disulphide (cf. Mills, Clark, and Aeschlimann, T., 1923, **123**, 2358) six products are formed and may be separated by fractional extraction with and crystallisation from water, benzene, or methyl alcohol, if necessary after conversion into the respective iodides. They are (i) bis-2-methylbenzothiazoline-1 : 1-spiran (Mills and Braunholtz, T., 1923, **123**, 2804); (ii) and (iii) pinacyanole and kryptocyanine (in very small amount); (iv) 2-*methyl*-1′-*ethylthio*iso*cyanine iodide*, m. p. 248—249°, which was prepared also from 4-methylquinoline ethonitrate; (v) 2-*methyl*-1′-*ethylthio*pseudo*cyanine iodide*, m. p. 254—256°, also prepared separately from 2-methylquinoline ethonitrate; and (vi) the main product (the quantity of which showed that condensation between two dissimilar molecules readily takes place), namely, 1 : 1′-*diethyl*-2 : 4′-*carbocyanine iodide*,

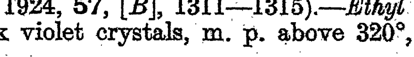


m. p. 240—241° (the crystals contain 1 MeOH). This substance is spectrometrically intermediate between pinacyanole and kryptocyanine.

The dicyanine, m. p. 244—252°, from 2 : 4-dimethylquinoline ethiodide (cf. Mikeska, Haller, and Adams, A., 1921, i, 54) was prepared by oxidising the base, in methyl-alcoholic solution, by exposure to the air. The absorption spectrum of this compound is almost identical with that of the above 2 : 4′-carbocyanine; this result and analytical figures show that the compound is 2′ : 4-*dimethyl*-1 : 1′-*diethyl*-2 : 4′-*carbocyanine iodide*. Presumably it is formed by the linking of 2 mols. of the ethiodide by means of a methenyl group furnished by disruptive oxidation of a portion of the material.

W. A. S.

Indigotin Group. IV. New Vat Dye Prepared from Indigotin and Ethyl Phenylacetate. T. POSNER and W. KEMPER (*Ber.*, 1924, **57**, [*B*], 1311—1315).—*Ethyl indigotinphenylacetate* (I), dark violet crystals, m. p. above 320°, is obtained by

(I.) 

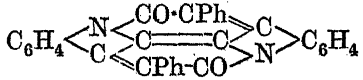
$$C_6H_4\left<\begin{matrix}N\\CO\end{matrix}\right>\overset{CO\cdot CPh}{C{=\!=}C}\left<\begin{matrix}C\\NH\end{matrix}\right>C_6H_4$$

protracted ebullition of powdered indigotin with a very large excess of ethyl phenylacetate. A substance, $C_{24}H_{17}O_2N$, m. p. 302°, which has not been investigated further, is obtained as by-product.

It is converted by reduction with sodium hyposulphite in the presence of sodium hydroxide and addition of benzoyl chloride to the solution into *ethyl benzoyldihydroindigotinphenylacetate*, m. p. 235°, and by benzoyl chloride in the presence of boiling pyridine into *ethyl benzoylindigotinphenylacetate*, m. p. 307° (decomp.), thus establishing the presence of the carbonyl and imino groups. Since it is transformed by protracted boiling with ethyl malonate into ethyl anhydrophenylacetylindigotinmalonate, identical with the product obtained by Posner and Pyl (A., 1923, i, 254) from ethyl indigotinmalonate and phenylacetyl chloride, it must contain the group $-CO{\cdot}C{:}C{\cdot}NH-$. The compound and ethyl indigotinmalonate are of peculiar interest since they can only be derived from the *trans* form of indigotin.

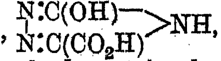
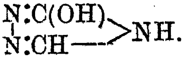
The constitution (II), assigned without stringent proof to Ciba-red B, is established by its production from ethyl indigotinphenylacetate and ethyl phenylacetate or phenylacetyl chloride. H. W.

(II.)

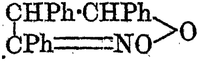
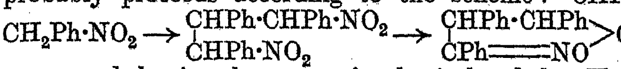


Quinazolines. XXXVII. Behaviour of Phthalic Anhydride with the Reactive Methyl Groups of certain Quinazolines. M. T. Bogert and F. P. Nabenhauer (*J. Amer. Chem. Soc.*, 1924, **46**, 1932—1936; cf. A., 1912, i, 214).—An attempt has been made to prepare dyes of the quinoline-yellow type by condensing several quinoxalines with phthalic anhydride and sulphonating the products. 2-Methyl-, 2 : 4-dimethyl-, 2-phenyl-, and 2-phenyl-4-methylquinazolines were prepared (in the main) by methods already described. 4-*Methylquinazoline*, pale yellow prisms, m. p. 36—37° (corr.), b. p. *ca.* 260° (corr.), was prepared by boiling 4-methylquinazoline-2-carbonamide with hydrochloric acid; *picrate*, m. p. 183·5° (corr.). These quinazolines when heated with phthalic anhydride at about 200° showed varying degrees of reactivity; the condensation was more rapid and complete when the methyl group was in the 2-position and the product was insoluble in dilute alkali. The condensation product (phthalone) from the 4-methylquinazolone was soluble in dilute alkali. Since only a small portion of the product from 2 : 4-dimethylquinazoline was soluble in alkali it appears that the 2-methyl had reacted rather than the 4-methyl group. The phthalones in all cases were amorphous and difficult to purify, those from 4-methyl- and 2-phenyl-4-methylquinazolines being incapable of purification. 2-*Methylquinazolinephthalone*, $C_{17}H_{10}O_2N_2$, is a yellowish-brown powder, soluble with a yellow colour in sulphuric acid and organic solvents. Its sulphonation product dyes silk a dull golden-yellow, not very fast to washing. 2 : 4-*Dimethylquinazolinemonophthalone*, $C_{18}H_{12}O_2N_2$, was obtained (impure) as a dark brown powder, insoluble in water and dilute alkali. The ammonium salt of the sulphonation product dyes silk a brown shade. The condensation product (purity, 80%) from 4-methylquinazoline and phthalic anhydride was strikingly different from the above phthalones, being insoluble in ethylbenzene and soluble in dilute alkali to a brown solution. Acids precipitated it as a brownish-yellow powder. It is a very strong dye, the dyeings (on silk), however, being less fast to washing than to light. 2-Phenyl-4-methylquinazoline formed only a small amount of condensation product with phthalic anhydride even after 8 hours' heating at 210°; a little of this was soluble in dilute alkali, the insoluble part (still containing unchanged quinazoline) on sulphonation giving a *product* which dyed silk orange. The dyes obtained appear to be decidedly inferior to quinoline-yellow.

A. C.

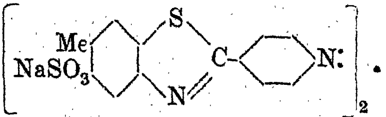
[Derivatives of *cyclo*Triazobutane.] R. STOLLÉ (*Ber.*, 1924, 57, [*B*], 1558).—The compound described by Diels and Behncke (this vol., i, 674) as *cyclo*triazomethene-4 : 4-dicarboxylic acid is identified as the hydroxytriazolecarboxylic acid,  $\begin{matrix}N{:}C(OH)\text{—}\\ |\\ N{:}C(CO_2H)\end{matrix}\!\!>NH$, whereas 2 : 4-carbonyl*cyclo*triazomethene is the hydroxytriazole,  $\begin{matrix}N{:}C(OH)\\ |\\ N{:}CH\text{—}\end{matrix}\!\!>NH$.

H. W.

***iso*Oxazoline Oxides. III. Triphenyl*iso*oxazoline Oxide.** E. P. KOHLER and G. R. BARRETT (*J. Amer. Chem. Soc.*, 1924, 46, 2105—2113).—By the condensation of nitrostilbene with phenylnitromethane in the presence of sodium methoxide (cf. Knoevenagel and Walter, A., 1905, i, 65), 3 : 4 : 5-*triphenyliso-oxazoline oxide*,  $\begin{matrix}CHPh{\cdot}CHPh\\ |\\ CPh\text{===}NO\end{matrix}\!\!>O$, m. p. 162°, is obtained, in which the only reactive group present is the system C : NO characteristic of *iso*oxazoline oxides (cf. this vol., i, 571, 998). The reaction probably proceeds according to the scheme: CHPh:CPh·NO₂+  $CHPh{:}CPh{\cdot}NO_2 + CH_2Ph{\cdot}NO_2 \longrightarrow \begin{matrix}CHPh{\cdot}CHPh{\cdot}NO_2\\ |\\ CHPh{\cdot}NO_2\end{matrix} \longrightarrow \begin{matrix}CHPh{\cdot}CHPh\\ |\\ CPh\text{===}NO\end{matrix}\!\!>O$, the dinitro compound having been previously isolated by Hein (A., 1911, i, 717). Triphenyl*iso*oxazole (Meisenheimer, A., 1922, i, 176) is the main by-product of the reaction and its formation is due to "stripping" of the *iso*oxazoline oxide by excess of sodium methoxide since this is rapidly converted into the *iso*oxazole on boiling with concentrated aqueous-alcoholic sodium hydroxide. Dilute bases have little action (cf. *loc. cit.*), and the mechanism of the "stripping" is not clear, as no evidence could be obtained of the intermediate formation of a ketolic oxime, $HO{\cdot}N{:}CPh{\cdot}CPh{:}CPh{\cdot}OH$. The oxide is not "stripped" by acetic acid, but loses water when heated alone, yielding *iso*oxazole and benzonitrile. Nitrous acid in acetic acid and permanganate in acetone do not attack the oxide, but with chromic acid in acetic acid phenyldibenzoylmethane (Meisenheimer, *loc. cit.*) was obtained. Bromine in acetic acid gave, besides *iso*oxazole, a small amount of a nitrogen-free *substance*, m. p. 125°. In other reactions also, the new *iso*oxazoline oxide shows marked differences from the oxides previously obtained, which contained acyl groups. With phosphorus pentachloride, it behaves like diphenylfuroxan, oxygen being removed, yielding 3 : 4 : 5-*triphenyl-*

iso*oxazoline*, m. p. 136—137°, which does not react with magnesium ethyl bromide, and is oxidised to triphenyl*iso*oxazole by chromic acid. Reduction with zinc and acetic acid converts the oxide into a stable *substance*, m. p. 188°, which yields an *acetyl* derivative, m. p. 100—110° (decomp.), a *benzoyl* derivative, m. p. 130°, and a *copper* derivative with cupric acetate; the structure 2-*hydroxy*-3 : 4 : 5-*triphenyl*iso*oxazoline* is accordingly assigned to it (cf. Posner, A., 1907, i, 55), the acidic properties being attributed to the NOH group. Concentrated sulphuric acid transforms this reduction product into (1) a 3 : 4 : 5-triphenyl*iso*oxazoline, m. p. 208°, isomeric with the product obtained by the action of phosphorus pentachloride on the *iso*oxazoline oxide ; (2) triphenyl*iso*oxazole, and (3) 3 : 4 : 5-*triphenyl*iso*oxazolidine*, m. p. 96°, which reacts with magnesium ethyl bromide, yields a nitroso compound, and is identical with the main product of the action of sulphuric acid on the oxide. Only small amounts of the *iso*oxazole are formed, and the relative amounts of this and the *iso*oxazolidine do not accord with a reciprocal oxidation–reduction reaction. Triphenyl*iso*oxazoline oxide reacts with a large excess of magnesium ethyl bromide, giving, in 50% yield, the above 2-hydroxy-3 : 4 : 5-triphenyl*iso*oxazoline. R. B.

Constitution of Columbia-yellow (Chloramine-yellow). M. T. Bogert and F. H. Bergeim (*Proc. Nat. Acad. Sci.*, 1924, **10**, 318—322).—Columbia-yellow is assigned the formula

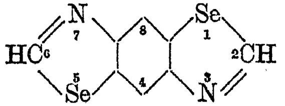


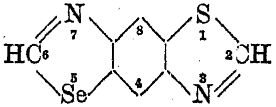
The position of the sulphonate groups is still in doubt. Specimens of the dye purified through the free sulphonic acid and its cerium salt give analyses and molecular weights agreeing with this formula. The dye was synthesised by reducing 2-*p*-nitrophenyl-6-methylbenzthiazole to the azo compound by means of zinc and alkali, and subsequently sulphonating; the product was physically, chemically, and tinctorially identical with Columbia-yellow. The lower homologue of this dye was prepared by oxidising sodium 2-*p*-aminophenylbenzthiazolesulphonate with sodium hypochlorite and proved to be a substantive dye of a lighter shade but very similar properties. Hence the methyl groups are not essential for the production of this type of dye, and in the usual method of preparation of Columbia-yellow by the action of sodium hypochlorite on sodium dehydrothio-*p*-toluidinesulphonate it is the amino group which is oxidised, and not, as has been suggested, the methyl group, giving rise to a stilbene derivative. The oxidation of the amino group may produce an azo compound, a quinone, a quinoneimine, a chloroimine, or a chloroamine. Since the purified dye contains no chlorine, the two latter are excluded. The resistance to oxidation and reduction exhibited by Columbia-yellow is an argument against quinone structure and further evidence in this direction was supplied by the observation that 2-*p*-hydroxyphenyl-

6-methylbenzthiazolesulphonic acid (prepared by diazotisation from dehydrothio-*p*-toluidinesulphonic acid) did not give a dye or a colour reaction when oxidised by sodium hypochlorite. S. S.

Selenium Organic Compounds. IV. Synthesis of Benzobis-selenazoles and Selenazolobenzothiazoles; New Heterocyclic Systems. M. T. Bogert and H. H. Hopkins (*J. Amer. Chem. Soc.*, 1924, **46**, 1912—1917).—The new heterocyclic types: (I) benzobis-selenazoles and (II) selenazolobenzthiazoles have been prepared by fusion of benzylideneaminobenzoselenazoles with selenium and with sulphur. 2 : 6-*Diphenyl*-p-β-*benzobis-selenazole*

(I.)





(II.)

lemon-yellow needles, m. p. 217°, was obtained in 17% of the theoretical yield by boiling 6-benzylideneamino-2-phenylbenzoselenazole with selenium. As proof of its structure it was also synthesised by fusing dibenzylidene-*p*-phenylenediamine with selenium. A mixture of the two products had the same m. p. It forms an unstable *acetyl chloride additive* product; a *nitro* derivative, m. p. 296·1—297·1°; a *dinitro* derivative, m. p. 332·4—333·4°. The nitro compound on reduction with tin and hydrochloric acid gives *amino*-2 : 6-*diphenyl*-p-β-*benzobis-selenazole* (yield 30%), orange needles, m. p. 279·4—281°; it formed a *benzylidene* derivative, m. p. 233·5—235·5°, when heated in boiling *n*-butyl-alcoholic solution with benzaldehyde. 2 : 6-*Diphenyl*-p-β-*selenazolobenzthiazole*, m. p. 220·4—221·5°, b. p. 345—350°/11 mm., was obtained as lustrous yellow needles from the mass formed on fusing 6-benzylideneamino-2-phenylbenzoselenazole with sulphur at 250—260°; the *tetrabromide* decomposed at 238—243°, and slowly on keeping; an *acetyl chloride additive* product melted at 224—225° with evolution of acetyl chloride; the *dinitro* derivative had m. p. 295—297°, and probably contained some mononitro derivative. The selenazolothiazole did not combine with methyl iodide in a sealed tube at 100°. One of the experiments for the preparation of the selenazolothiazole resulted in a 25% yield of a new *base*, $C_{27}H_{18}N_2S_2Se$, long, straw-coloured needles, m. p. 5° higher than the selenazole and quite distinct from it. The base gave a *dinitro* derivative, m. p. 283°, which on reduction yielded the *compound* $C_{27}H_{20}N_4SSe$, brownish-yellow needles, m. p. 305° (decomp., with evolution of hydrogen sulphide). The character of the base was not ascertained, since, although numerous attempts were made, it could not be formed again. 6-*Furfurylideneamino*-2-*phenylbenzoselenazole*,

$$C_{18}H_{12}ON_2Se,$$

yellow needles, m. p. 147·5°, was prepared by heating 6-amino-2-phenylbenzoselenazole with excess of furfuraldehyde. Attempts to combine it with selenium were unsuccessful, as it charred below the m. p. of selenium. No pure product was obtained on heating the furfurylideneamino compound with sulphur. A. C.

Naphthalene and its Derivatives. N. VOROSHCOV (*Bull. Soc. chim.*, 1924, [iv], **35**, 996—1021).—The dissociation in aqueous solution of the *sodium hydrogen sulphite* compounds of benzeneazo-α-naphthol, yellow needles, benzeneazo-β-naphthol ($+2H_2O$), brilliant golden-yellow spangles, obtained by the action of sodium hydrogen sulphite on the pure azo compound, and of 5-hydroxynaphthaleneazophenol, obtained by coupling phenol with the diazotised sodium hydrogen sulphite compound of 1 : 5-aminonaphthol, has been examined. In all cases, dissociation into azo compound and sulphite increases with the dilution and with the alkalinity of the solution, a very small increase in the number of hydroxyl ions producing a marked increase in the dissociation, whilst in acid solution the dissociation is very slightly retarded, and decreases slightly with increasing concentration of the acid. These results show that the three sulphite compounds have a similar structure and are to be regarded essentially as additive compounds, in opposition to Bucherer's views (A., 1904, i, 309). The formation of such additive compounds will depend on the nature of the conjugated system and the positions of the substituents in the ring, the systems –C(OH):C·C:CX– and –C(OH):CX– favouring the reaction, whilst the systems –C(OH):CH·CX:CH– and –CH:C(OH)·CH:CX–, existing in the 3-substituted α-naphthols and 4-substituted β-naphthols, do not favour addition, and consequently the Bucherer reaction does not take place (cf. Meyer and Lenhardt, A., 1913, i, 704, 723). The different behaviour of the two amino groups in 1 : 5- and 1 : 8-naphthylenediamine with sodium hydrogen sulphite finds an explanation in the different character of the two benzene rings in the naphthalene molecule; one ring behaves as a conjugated olefinic system and yields the additive compound, leading to the naphthol, whilst the other behaves as an aromatic ring system and yields no additive product. The alkylation of the naphthols is similarly explained as due to the formation of an intermediate additive compound, and the conversion of naphthols into naphthylamines and the reverse reaction in the absence of sulphites are given a similar interpretation. The naphthols and naphthylamines from this point of view are intermediate in reactivity between the reactive conjugated open-chain compounds, such as ethyl acetoacetate or β-aminocrotonate, and the typical aromatic phenols and amines of the benzene series. The readiness with which phenols, such as nitrosophenol, phloroglucinol, and nitroso-β-naphthol, which are capable of tautomeric change, are converted into amines also supports the theory (cf. Fuchs and Stix, A., 1922, i, 451; Friedländer, A., 1921, i, 443).

R. B.

Optically Active Dyes. II. Adsorption, Absorption Spectra, and Rotation. W. R. BRODE and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, **46**, 2032—2043).—In continuance of their projected investigation of the question whether the absorption of dyes by animal or vegetable fibres is a physical or chemical process, using the previously described β-naphthol derivatives of *d*-, *l*-, and *dl*-*p*-diazobenzamidophenylacetic acid (Ingersoll and Adams, A., 1923, i, 200), the authors have established that the adsorption of the two optically active forms of the dye by inactive adsorbing agents, such as charcoal and ball-clay, is identical, but is rather less than that of the racemic form, which also exists more in a colloidal state than do the *d*- and *l*-compounds. The absorption spectra of the active forms of the dye show bands of the same frequency, and variation of the hydrogen-ion concentration of the solutions changes the intensity, but not the wave-length of the bands (cf. A., 1922, ii, 602). Within the range of hydrogen-ion concentration change caused by the addition of common adsorbing agents, the change of colour of the active forms of the dye and the possible difference in the intensity is negligible as far as colorimetric determinations are concerned. Beer's law is valid for the dilute solutions used in these experiments and as far as studied the rotation of the two active dyes is normal. On long standing with sodium hydroxide, racemisation of the active forms takes place, and from saturated solutions of the active forms, the less soluble *dl*-form separates. In view of these facts, it is concluded that any difference in the adsorption of the *d*- and *l*-forms of the dye in the dyeing experiments may be taken as evidence of chemical reaction in the dyeing process. R. B.

Influence of Sulphur on the Colour of Azo Dyes. D. G. FOSTER and E. E. REID (*J. Amer. Chem. Soc.*, 1924, **46**, 1936—1948).—By methods very similar to those employed for the para-analogues (cf. this vol., i, 95), a number of *o*-aminophenyl alkyl sulphides have been made by condensing sodium *o*-nitrothiophenoxide with alkyl halides and reducing the nitro compound with iron and acetic acid. Diamines of the type $(NH_2\cdot C_6H_4\cdot S\cdot)_2R$, with sulphur have been made in the same way from alkylene dihalides. In many cases, the *o*-nitrophenyl alkyl sulphides were not isolated but reduced at once to the corresponding amino compounds, but the following were prepared in the pure state: *ethyl*, b. p. 149—150°/15 mm., *propyl*, b. p. 172—174°/7 mm., *allyl*, m. p. 54°, the respective yields being 46, 64, 32% of the theoretical. The *allyl sulphide*, m. p. 38—39°, and the cyclo*hexyl sulphide*, m. p. 56—57° of the para-analogue were also prepared. All the amines of this series are oils which decompose below their boiling points, even under diminished pressure. They were isolated as hydrochlorides as white, crystalline solids, $R\cdot S\cdot C_6H_4\cdot NH_2,HCl$ (the figures represent the % of the theoretical yield on the alkyl halide). *Methyl* (74), *ethyl* (73), *propyl* (54), iso*propyl* (99), *butyl* (55), iso*butyl* (72), iso*amyl* (71), cyclo*hexyl* (32), *allyl* (75). *Allyl*- and cyclo*hexyl*-p-*aminophenyl sulphides* were isolated as sulphates in 45 and 93% of the theoretical yields, respectively. The following o : o′-*dinitrodiphenyl disulphides* are described: $(C_6H_4\cdot NO_2)_2S_2CH_2$, m. p. 170° from methylene iodide; $(C_6H_4\cdot NO_2)_2S_2(CH_2)_2$, m. p. 205°, from ethylene dibromide; $(C_6H_4\cdot NO_2)_2S_2(CH_2)_3$, m. p. 140°, from trimethylene bromide, and $NO_2\cdot C_6H_4\cdot S\cdot C_2H_4\cdot S\cdot C_2H_4\cdot S\cdot C_6H_4\cdot NO_2$ (a trisulphide), m. p. 107—108°, from *pp*-dichlorodiethyl sulphide and sodium *o*-nitrothiophenoxide. The last four substances are very sparingly soluble yellow solids. On reduction the corresponding diamines were obtained as brown oils; their hydrochlorides (which hydrolyse very rapidly) could not be obtained crystalline, but were precipitated from alcohol by means of ether:

$$(C_6H_4{\cdot}NH_2)_2S_2CH_2,2HCl,\ (C_6H_4{\cdot}NH_2)_2S_2(CH_2)_2,2HCl,$$
$$(C_6H_4{\cdot}NH_2)_2S_2(CH_2)_3,2HCl \text{ and } (C_6H_4{\cdot}NH_2{\cdot}S{\cdot}C_2H_4)_2S,2HCl$$

were obtained in 91, 21, 89, and 90% of their respective theoretical yields. For the purpose of demonstrating the effect of the sulphone group (on the character of the dyes described below), as compared with the sulphur atom alone, the following *o*-nitrophenylsulphones (white, crystalline solids) were prepared by the method described for the para compounds: $NO_2{\cdot}C_6H_4{\cdot}SO_2Me$, m. p. 104—105°; $NO_2{\cdot}C_6H_4{\cdot}SO_2Pr$, m. p. 50°; $(NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH_2)_2CH_2$, 156—157° in 65, 86, and 72% of the respective theoretical yields. The *o*-nitrophenylmethyl and propyl sulphones gave the corresponding *amines*, $NH_2{\cdot}C_6H_4{\cdot}SO_2Me$, an oil, and $NH_2{\cdot}C_6H_4{\cdot}SO_2Pr$, m. p. 50°, in 69 and 53% of the theoretical yields, but the trimethylene nitrosulphone was reduced to the amine of the disulphide,

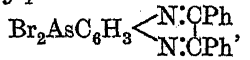
$$NH_2{\cdot}C_6H_4S(CH_2)_3{\cdot}S{\cdot}C_6H_4{\cdot}NH_2.$$

One of the sulphones of the para series behaved similarly. Dyes were made from all the above *o*-nitrophenyl alkyl sulphides and disulphides and sulphones by diazotisation and coupling with R-salt; only the free mercaptan, $NH_2{\cdot}C_6H_4{\cdot}SH$, failed to couple and give a dye. They dyed wool red, orange, and yellow shades. A comparison with similar sulphur-free dyes from known intermediates gave; –Me *deep salmon*, –OMe *carmine*, –SMe *yellowish-red*, $-SO_2Me$ *orange*, *i.e.*, in the dyes containing sulphur the characteristic wave-length moves from the red towards the yellow whilst the methoxyl group appears more strongly bathochromic than the alkyl sulphide. In general, the bathochromic effect is much less marked than with sulphur in the para position. In the simple alkyl sulphides, increase in the molecular weight of the alkyl group attached to the sulphur produces a general hypsochromic effect, showing a periodicity in colour similar to that shown in certain physical constants of aliphatic homologous series. The dyes formed from the *o*-diamine bases are markedly different from the benzidine dyes both as to colour and in the fact that none of the ortho dyes are substantive. A hypsochromic effect is shown with reference to the sulphur-free dye when the two sulphur atoms are separated by only one carbon atom. Increasing separation and the introduction of a third atom of sulphur show a bathochromic influence with respect to the other sulphur dyes of the series. The colour relation to the sulphur-free dye is difficult to place. A. C.

Formation of Dyes on Animal Fibres by Reaction of the Material Itself. J. Groot (*Chem. Weekblad*, 1924, **21**, 450—455).—Wool, silk, hair, and other animal fibres react with nitrous acid, acquiring an intense yellow colour, which may be discharged by sunlight, heating, or the action of alkalis. The action is slow, requiring about 20 hours in the cold. After treatment and thorough washing, the fabric on treatment with phenols or amines acquires distinctive colours. The coupling takes place in faintly acid or alkaline solutions, and the colours are fast to light and washing, but not to acids and alkalis. Subsequent treatment with metallic salts or with dichromate modifies the colours obtained; the mechanical strength of the fabrics is not adversely affected. The reaction appears to be a true diazotisation of the amino groups of the fibre proteins. S. I. L.

Condensation Products of Aminoarsanilic Acid (3 : 4-Diaminophenylarsinic acid). W. L. LEWIS, P. L. CRAMER, and R. S. BLY (*J. Amer. Chem. Soc.*, 1924, **46**, 2058—2065).—With a view to study their therapeutic properties a number of arsinated quinoxalines have been prepared by the condensation of 3 : 4-diaminophenylarsinic acid with *o*-diketones. The condensation of 3 : 4-diaminodiphenylarsinic acid with cyanogen and with ω-bromoacetophenone yields dihydroquinoxalines, but with monocarbonyl compounds, such as benzaldehyde, a series of arsenated Schiff's bases is obtained: $H_2O_3As\cdot C_6H_3(NH_2)_2+2PhCHO=2H_2O+AsH_2O_3\cdot C_6H_3(N:CHPh)_2$. The behaviour of ethyl acetoacetate is exceptional and a condensation product of 1 mol. of amino-acid with 1 mol. of acetone is obtained: $AsH_2O_3\cdot C_6H_3(NH_2)_2+Ac\cdot CH_2CO_2Et \longrightarrow EtOH+CO_2+AsH_2O_3\cdot C_6H_3(NH_2)(N:CMe_2)$, a product which cannot be obtained directly from acetone.

3 : 4-Diaminodiphenylarsinic acid, obtained by Bertheim's method (A., 1911, i, 1055), using Jacobs and Heidelberger's method of reduction with ferrous hydroxide (A., 1919, i, 50), with diacetyl in absolute alcohol, yields 2 : 3-*dimethylquinoxaline*-6-*arsinic acid*, lustrous, pink flakes, m. p. 212—215° (decomp.). Similarly, in boiling methyl-alcoholic solution benzil gives 2 : 3-*diphenylquinoxaline*-6-*arsinic acid*, a white or slightly yellow substance (yield 64%), which on treatment with 50% hydrobromic acid in boiling acetic acid yields 2 : 3-*diphenylquinoxaline*-6-*arsenious bromide*,

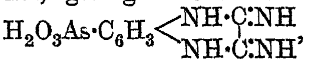


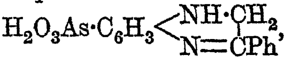
$$Br_2AsC_6H_3{<}\begin{matrix}N:CPh\\ |\\ N:CPh\end{matrix},$$

lustrous, yellow plates, m. p. 232°; the corresponding *dihydroxide* is white and the *chloride* has m. p. 185—187°; the *iodide* is described. The *dihydroxide* condenses with chloroacetic acid in alkaline aqueous-alcoholic solution (cf. Adams and Quick, A., 1922, i, 600), yielding 2 : 3-*diphenylquinoxaline*-6-*arsinoacetic acid*,

$$CO_2H\cdot CH_2\cdot AsO_2H\cdot C_{20}H_{13}N_2,$$

m. p. 122—125° (decomp.). 3 : 4-Diaminodiphenylarsinic acid and dinitrobenzil (Barnett and Kay, A., 1922, i, 844) in methyl alcohol give (yield 75%) 2 : 3-*di*-m-*nitrophenylquinoxaline*-6-*arsinic acid*, m. p. above 230° and giving a deep red solution in alkali. Similarly with anisil, prepared from oxalyl chloride and anisole by Staudinger's method (A., 1912, i, 567), is obtained, in 61% yield, 2 : 3-*di*-p-*methoxyphenylquinoxaline*-6-*arsinic acid*, light yellow needles, and with furil, 2 : 3-*difurylquinoxaline*-6-*arsinic acid*, m. p. above 250°. In glacial acetic acid are obtained similarly, from phenetil (*pp'*-diethoxybenzil), m. p. 150—151° (cf. Vorländer, A., 1911, i, 865), prepared by Staudinger's method, 2 : 3-*di*-p-*ethoxyphenylquinoxaline*-

6-*arsinic acid*, light yellow (yield 84%); from piperil (3 : 4-dimethylenedioxy-3′ : 4′-methylenedioxybenzil, 2 : 3-*di*-3 : 4-*methylenedioxyphenylquinoxaline*-6-*arsinic acid*, yellow crystals (yield 92%); and from tetramethyldiaminobenzil, 2 : 3-*di*-p-*dimethylaminophenylquinoxaline*-6-*arsinic acid*, yellow powder, m. p. above 260° (yield 45%). 3 : 4-Diaminophenylarsinic acid and cyanogen combine in methyl alcohol, giving 2 : 3-*di-imino*-1 : 4-*dihydroquinoxaline*-6-*arsinic acid*,  $H_2O_3As\cdot C_6H_3<\begin{matrix}NH\cdot C{:}NH\\ NH\cdot C{:}NH\end{matrix}$, orange powder, m. p. 200—205° (decomp.), and ω-bromoacetophenone similarly yields 3(?)-*phenyl*-1 : 2-*dihydroquinoxaline*-6-*arsinic acid*,



$$H_2O_3As\cdot C_6H_3<\begin{matrix}NH\cdot CH_2\\ N{=}CPh\end{matrix},$$

orange crystals, m. p. above 250°.

[With E. A. LARSEN.]—With ethyl acetoacetate in boiling methyl alcohol, 3 : 4-diaminodiphenylarsinic acid gives in 88% yield 4-*dimethylmethyleneamino*-3-*aminophenylarsinic acid*, m. p. above 260°. Similarly, aldol gives (yield 26%) 3 : 4-*di*-γ-*hydroxybutyleneaminophenylarsinic acid*, $H_2AsO_3\cdot C_6H_3[N{:}CH\cdot CH_2\cdot CHMe(OH)]$, m. p. below 260°; with crotonaldehyde is obtained 3 : 4-*dicrotonylideneaminophenylarsinic acid*, $H_2AsO_3\cdot C_6H_3(N{:}CH\cdot CH{:}CHMe)_2$, m. p. above 260°; with benzaldehyde, 3 : 4-*dibenzylideneaminophenylarsinic acid*, yellow, m. p. above 250° (yield 28%); with *o*-methoxybenzaldehyde, 4-o-*methoxybenzylideneamino*-3-*aminophenylarsinic acid*, m. p. above 250°; with anisaldehyde, 4-p-*methoxybenzylideneamino*-3-*aminophenylarsinic acid*, yellow powder, and with piperonal, 4-*piperonylideneamino*-3-*aminophenylarsinic acid*,

$$H_2AsO_3\cdot C_6H_3(NH_2)(N{:}CH\cdot C_6H_3\cdot O_2CH_2).$$

With the object of obtaining a substance with pharmacological properties analogous to tryparsamide (Jacobs and Heidelberger, A., 1920, i, 108), 3 : 4-diaminodiphenylarsinic acid in sodium hydroxide was condensed with chloroacetamide, giving (yield 58%) 4(?)-*acetamidoamino*-3-*aminophenylarsinic acid*,

$$H_2AsO_3\cdot C_6H_3(NH_2)(NH\cdot CH_2\cdot CO\cdot NH_2),$$

decomp. 220—232°. R. B.

Arsenobenzene Derivatives. A. CONTARDI and U. CAZZANI (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 329—338; from *Chem. Zentr.*, 1924, i, 2512).—3 : 3′-Diamino-4 : 4′-dihydroxyarsenobenzene (salvarsan) forms with dilute (2·5—20%) solutions of dextrose a *monoglucoside*, $[{:}As\cdot C_6H_3(NH_2,HCl)\cdot O\cdot C_6H_{11}O_5]_2,2H_2O$, a yellow powder having $[\alpha]_D^{20}$ −137·1°. It forms a *picrate* with 2 mols. of picric acid. The *diglucoside*,

$$OH\cdot C_6H_3(NH_2)\cdot As{:}As\cdot C_6H_3(OH)\cdot NH\cdot C_6H_{11}O_5,$$

formed with more concentrated solutions of dextrose is similar to the monoglucoside. Similar glucosides are given by galactose, α-arabinose, and rhamnose. Neosalvarsan, "neojacol," and "sulpharsenol" also yield glucosides with dextrose. Ethylene glycol yields with salvarsan a *compound*

$$OH\cdot C_6H_3(NH_2)\cdot As{:}As\cdot C_6H_3\cdot NH\cdot CH_2\cdot CH_2\cdot OH.$$

G. W. R.

New Organic Arsenic Compounds. O. MARGULIES (Brit. Pat. 220668).—When mono- or poly-amino derivatives of aromatic aldehydes or ketones, or of mixed aliphatic-aromatic ketones, are diazotised and treated with an arsenite in aqueous solution, the carbonyl group is not attacked and arsinic acids of therapeutic value are obtained. Preparations, by this method, of the following compounds are described: *Nitroxyacetophenonearsinic acid*, m. p. about 200°; *acetophenone*-p-*arsinic acid*, m. p. about 176°; *benzophenone*-p-*arsinic acid*, m. p. 195—197°; *benzophenone*-4 : 4'-*diarsinic acid*, m. p. 236°; p-*aldehydophenylarsinic acid*; 3-*hydroxybenzophenone*-4'-*arsinic acid*, m. p. 180°; 4-*acetamidobenzophenone*-3'-*arsinic acid*, m. p. 253°; ω-*phthalimidoacetophenone*-p-*arsinic acid*, m. p. not below 270°; *phenyl*-p-*arsinic acid benzyl ketone*, m. p. 160° (decomp.); *propiophenone*-p-*arsinic acid*, m. p. not below 275°; and *nitro*-p-*aldehydophenylarsinic acid*, decomp. 130°. [Cf. *B.*, Nov. 28th.] F. G. W.

Preparation of *o*-Nitrodiphenylarsinic Acid. E. SAKELLARIOS (*Ber.*, 1924, **57**, [*B*], 1514—1515).—*o*-Nitrodiphenylarsinic acid is prepared in 87% yield by the addition of a solution of phenylarsenious oxide in sodium hydroxide and sodium acetate to a diazotised solution of *o*-nitroaniline in hydrochloric acid. H. W.

Preparation and Properties of Diphenyl-4 : 4'-diarsinic Acid. [MISS] A. E. HILL (*J. Amer. Chem. Soc.*, 1924, **46**, 1855—1857).—It has been sought to extend the inhibiting effect on the growth of certain bacilli possessed by organic substances having the so-called benzidine configuration (cf. Lewis, *J. Exp. Med.*, **25**, 441) by combining it with other substances which are known to be therapeutically active in other directions. *Diphneyl*-4 : 4'-*diarsinic acid* was prepared by the Bart reaction from tetrazotised benzidine (cf. A., 1913, i, 115, 415). The acid forms white crystals, is characterised by extreme inertness and stability, and is insoluble in the common organic solvents; it dissolves in boiling water to the extent of 0·1%, in hot sulphuric acid and in hot glycerol without change, and is not attacked by bromine or iodine. It is not sulphonated by fuming sulphuric acid. It is tetrabasic and differs from the diphenylarsinic-*o*-arsinic acid of Kalb (cf. A., 1921, i, 375). The *tetrasodium* salt, white, columnar crystals, contained $14H_2O$ (cf. following abstract). A. C.

Diarsonodiphenyl [Diphenyl-4 : 4'-diarsinic acid] and Derivatives. W. W. BAUER and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, **46**, 1925—1931).—Various arsenic derivatives of diphenyl of possible therapeutic value have been prepared. Tetrazotised benzidine and alkaline sodium arsenite afforded diphenyl-4 : 4'-diarsinic acid, not melting below 300°, being practically insoluble in ordinary solvents. A brown by-product, not obtained pure, appears to be 4-hydroxydiphenyl-4'-arsinic acid. Attempts to nitrate the diarsinic acid were unsuccessful, complex oxidation resulting. It was, however, found possible to prepare, from

3 : 3′-dinitrobenzidine, 3 : 5′-*dinitrodiphenyl*-4 : 4′-*diarsinic acid* (yield, 65%), a light yellow, insoluble solid. The amino groups in 2 : 2′-dinitrobenzidine could not be readily displaced by arsinic acid groups. 3 : 5-*Diaminodiphenyl*-4 : 4′-*diarsinic acid* was obtained as a yellowish-white powder (79% yield), by the reduction of the corresponding dinitro compound with alkaline ferrous hydroxide. It showed all the properties of aminoarsinic acids of the benzene series, and gave a white *diacetyl* derivative. Tetrazotised 3 : 5′-diaminodiphenyl-4 : 4′-diarsinic acid couples with 2 mols. of H-acid to form a dye, $C_{32}H_{26}O_{20}N_6S_4As_2$, of the trypan-blue type, a bronze-coloured solid soluble in water to a bluish-red solution. *o*-Tolidine afforded similar compounds : 3 : 5′-*dimethyldiphenyl*-4 : 4′-*diarsinic acid* (yield, 44%) is a white powder, insoluble in water and organic solvents, and does not melt below 310°. On oxidation with alkaline permanganate, it gives 3 : 5′-*dicarboxydiphenyl*-4 : 4′-*diarsinic acid*, fine, white crystals insoluble in water. Compounds containing an arsinic acid radical attached to one ring and a hydroxyl or amino group attached to the other were also prepared. The best method consisted in forming the tetrazo compound, coupling one diazonium group with a component which could be reduced to an amino group, and then replacing the second diazonium group by an arsinic acid radical. 4-*Aminodiphenyl*-4′-*arsinic acid* was prepared in this manner, using H-acid for the coupling. After the introduction of the arsinic acid group, the product is reduced with sodium hyposulphite and the resulting 4 : 4′-di-*p*-aminodiphenylarsenobenzene, $(NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}As{:})_2$, separated from the amino-H-acid, making use of its insolubility in alkali. The arseno compound, when oxidised with alkaline hydrogen peroxide, gives the aminoarsinic acid (*acetyl* derivative, a white solid). Pharmacological tests showed the acetyl derivative to have about the same toxicity as arsanilic acid, whilst 3 : 5′-diaminodiphenyl-4 : 4′-diarsinic acid is much less toxic (cf. preceding abstract).

A. C.

Complex Organic Compounds of Mercury. W. SCHOELLER (D.R.-P. 387850; U.S. Pat. 1457675; from *Chem. Zentr.*, 1924, i, 2397—2398).—Complex organic compounds of mercury are prepared having the general formulæ XHg·R·R·HgX and

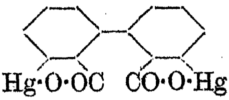
$$XHg{\cdot}R{\cdot}B{\cdot}R{\cdot}HgX,$$

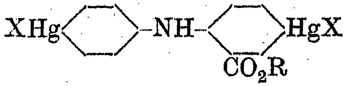
respectively, where X denotes a simple group such as Cl, SO_4, or OAc and R and B complex organic groups. Such compounds when treated with ammonium sulphide yield cyclic compounds in which the two mercury atoms are connected by a sulphur atom. Diethyl diallylmalonate gives with mercuric acetate a complex *ester*, which yields on treatment with sodium chloride solution and subsequent hydrolysis a *dicarboxylic acid*,

$$(CO_2H)_2{:}C(CH_2{\cdot}CH[HgCl]{\cdot}CH_2{\cdot}OEt)_2.$$

Complex mercury compounds may also be prepared with diallylbarbituric acid and ethyl diallylacetate, respectively. Diethyl *o*-phenylenediacrylate yields with mercuric acetate a complex *mercury compound*, $C_6H_4(CH[OMe]{\cdot}CHgX{\cdot}CO_2Et)_2$. From diphenic acid and mercuric acetate *bismercuroxydiphenic anhydride* (I) is

(I.)





(II.)

obtained. Similarly, ethyl diphenylamine-2-carboxylate yields the complex type (II). G. W. R.

Ring Formation in Additive Compounds. I. Cyclic Molecular Compounds of the Stannic Halides. W. HIEBER (*Annalen*, 1924, **439**, 97—131; cf. Pfeiffer and others, A., 1917, i, 205, etc.; and "Organische Molekülverbindungen," Stuttgart, 1922).—Molecular-weight determinations (by the cryoscopic method in ethylene bromide solution) show that the compounds,

$$(R{\cdot}CO_2R')_2,SnCl_4,$$

formed by union of various esters with stannic chloride, are dissociated to varying degrees in solution. Those from the esters of benzoic acid are almost completely dissociated, but the ethyl β-phenylpropionate compound is more stable and that from ethyl cinnamate is hardly split up at all. Stability here runs parallel with melting-point and resistance to attack by moisture. The extent to which dissociation takes place depends in each case on the concentration and also on the nature of the solvent; nitrobenzene is more active than ethylene bromide, although even in the former the benzaldehyde–stannic chloride additive compound is stable.

The above determinations were made as a preliminary to an investigation of the molecular structure of the compounds obtained from stannic halides and the esters of dibasic acids and related compounds. These compounds are formed by union of equimolecular proportions of the components, and Pfeiffer's formula (*loc. cit.*), which is unsatisfactory for stereochemical reasons, is shown to be incorrect. Molecular-weight determinations indicate that in every case the compounds have the formula

$$[(CH_2)_n(CO_2R)_2,SnCl_4]_2;$$

they are dissociated to varying degrees in solution, but the observed molecular weight is always greater than that required by the simple formula.

The following new compounds are described (a number of others, already described by Pfeiffer and others, were also investigated); all were prepared in a special apparatus designed to secure anhydrous conditions. The *additive* compounds of stannic chloride with various esters have melting points as follows: methyl oxalate, 86°; methyl malonate (needles), 154°; methyl adipate (needles), 132°; methyl pimelate, 116°; methyl suberate (prisms or needles), 110°; methyl azelaate and methyl sebacate, 95° and 90°, respectively. The existence of these compounds by itself, apart from the above results, suggests that they cannot be formed by union molecule for molecule as it is difficult to imagine the two so widely separated carbonyl groups being associated with the auxiliary valencies of the one tin atom. Further, similar results were obtained with other compounds: methyl and ethyl fumarates yield stannic chloride *additive* compounds of m. p. 91—92° and 81—82°, respectively; methyl and ethyl maleates yield similar, but quite distinct, compounds, m. p. 123° and 114—115°, respectively. These substances regenerate the parent ester unchanged when treated with water; the formation of the additive compounds is therefore independent of the configuration and is not the result of intramolecular change. A molecular-weight determination on the ethyl fumarate compound confirmed the formula

$$[C_2H_2(CO_2Et)_2,SnCl_4]_2.$$

Similar *compounds* are formed by methyl phthalate (m. p. 146°), methyl *iso*phthalate (needles, m. p. 71°), methyl terephthalate (m. p. 137°), and ethyl terephthalate (m. p. 65°). α-Stilbenediol diacetate yields a *compound*, m. p. 122° (decomp.), the β-isomeride a different *compound*, m. p. 98°; and the *cis*- and *trans*-forms of dibenzoylethylene both give analogous *compounds*, that from the former being very unstable, and that from the latter having m. p. 120° (decomp.).

Stannic chloride has the normal molecular weight in ethyl malonate, succinate, or glutarate and the compound of stannic chloride and ethyl oxalate is completely dissociated in these solvents.

Analogous *compounds* are formed by stannic bromide; thus, with methyl malonate, leaflets, m. p. 69°; with methyl adipate, m. p. 45°; ethyl maleate, scales, m. p. 35—36°; methyl phthalate, m. p. 20°. Similar observations to those described above were made on these compounds.

Both ethyl fumarate and maleate combine with antimony pentachloride, the *compounds*, $C_2H_2(CO_2Et)_2,2SbCl_5$, having m. p. 140° (decomp.) and 120°, respectively. The analogous *compound* from ethyl terephthalate forms leaflets.

Certain other observations are recorded, for details of which the original should be consulted. W. A. S.

Biochemistry.

Gas and Electrolyte Equilibria in the Blood. VII. Effect of Carbon Monoxide on Acidity of Hæmoglobin. A. B. HASTINGS, J. SENDROY, jun., C. D. MURRAY, and M. HEIDELBERGER (*J. Biol. Chem.*, 1924, **61**, 311—335).—The experiments on the base-binding power of oxygenated and reduced hæmoglobin (this vol., i, 1008) have been extended to carbon monoxide–hæmoglobin, which was found to behave identically with oxyhæmoglobin. Electrometric titration curves for reduced hæmoglobin and carbon monoxide–hæmoglobin over the range p_H 6·2—8·6 have been obtained. It is concluded that the increase in base-binding power of hæmoglobin, which occurs to the same extent on combination with either oxygen or carbon monoxide, is due to an increase in the dissociation constant of one labile carboxyl group in the hæmoglobin molecule. C. R. H.

Protein Coagulation in Drops. V. Influence of Genus, Sex, and Age of Animals on the Precipitability of the Blood-serum. E. Přibyl, V. Šuk, and J. Zlámal (*Biochem. Z.*, 1924, **148**, 529—540).—The precipitability of horse, ox, and pig sera by various reagents (formaldehyde, alcohol, acids, various metallic salts, pyrogallol, tannin) differs in type and in range as studied by Bečka's drop method, and shows further variations with the age and sex of the animal. The sera of castrated animals are less readily precipitated than is the serum of normal animals. J. P.

Protein Coagulation in Drops. VI. Influence of Nitrogen Compounds on the Precipitation. J. Bečka and A. Šimánek (*Biochem. Z.*, 1924, **149**, 150—157).—Amino-acids inhibit, urea increases the precipitating action of copper sulphate on 1% horse-serum solutions; 1% ox-serum is more readily precipitated by cupric, zinc, and ferrous salts in the presence of amino compounds than in their absence. The action of the amino group in these respects is not affected by alterations in the concentration of the protein or of the sodium chloride present. The action of amino nitrogen in increasing the precipitation of horse-serum by tannin can be utilised for the detection of the former in dilutions as great as $M/10,000$. J. P.

Chlorides of Serum, Blood, and Corpuscles in Pathological Conditions. H. C. Gram (*J. Biol. Chem.*, 1924, **61**, 337—343).—A study of cases of various diseases shows that a deviation from the normal in the concentration of chloride in the serum is accompanied by a corresponding percentage deviation in the chloride of the whole blood; assuming that corpuscle chlorides vary directly with serum chlorides, it is possible to calculate the chloride concentration of the whole blood from that of the serum together with a determination of the corpuscle volume. The observed results agree with those calculated in this manner to within 3%. C. R. H.

Refractometric and Interferometric Quantitative Analysis. II. Blood-serum. J. Bečka (*Z. physiol. Chem.*, 1924, **139**, 52—56).—When serum is mixed with dilute sodium chloride, the refraction of the mixture is usually smaller than that calculated. The deviations from the calculated value differ with different species and depend on the age of the animal from which the serum was obtained and also on the age of the serum itself. E. S.

Refractometric and Interferometric Analysis. III. Changes in the Refractive Power of Serum. J. Bečka and V. Zemanec (*Z. physiol. Chem.*, 1924, **139**, 97—106).—Under the influence of carbon dioxide, warmth, and light, the refractive index of sterile serum is increased on standing for 24 hours; in presence of oxygen, it is diminished; these changes are greater in ox-serum than in horse-serum and are more rapid in the serum of young than of old animals. C. R. H.

Surface Tension of Serum. X. Thickness of a Unimolecular Layer of Serum. P. L. Du Noüy (*J. Exp. Med.*, 1924, **40**, 133—149; cf. this vol., i, 900).—Consideration of the minimum value of the surface tension in relation to the dilution of a serum solution leads to the supposition that a unimolecular layer exists at a certain dilution. The thickness of the protein molecule is then calculated to be $35{\cdot}4 \times 10^{-8}$ cm. The result for crystalline egg-albumin was $52{\cdot}8 \times 10^{-8}$ cm. Chemical Abstracts.

Nature of Blood-sugar. W. Denis and H. V. Hume (*J. Biol. Chem.*, 1924, **60**, 603—612).—In a repetition of the work of Winter and Smith (A., 1923, i, 513), the authors have failed to observe any decrease in the power of normal blood filtrates on keeping for 3 days to decolorise permanganate. Although changes in the rotatory power of such filtrates have been occasionally observed, these have always coincided with the growth of mould in the polarimeter tube and have never occurred when sodium or potassium fluoride has been used as anti-coagulant. Thus no support is given to the view that γ-glucose is present in normal blood. E. S.

Blood-sugar and Gastric Hunger Contractions. E. Bulatao and A. J. Carlson (*Amer. J. Physiol.*, 1924, **69**, 107—115).—Intravenous injection of dextrose inhibits gastric hunger contractions which, in insulin hypoglycæmia, increase at a blood-sugar concentration of 0·07—0·08%. Dextrose, but not lactose, inhibits the gastric tetany of hypoglycæmia. A. A. E.

Hypoglycæmia and Acidosis. F. B. Talbot, E. B. Shaw, and M. E. Moriarty (*J. Amer. Med. Assoc.*, 1924, **83**, 91—93).—Acidosis during fasting is accompanied by low blood-sugar concentrations (45 mg. per 100 c.c.). A certain proportion of the fatty acids is not completely oxidised, and the keto-acids thus produced deplete the alkali reserve; this is accompanied by a shift of the p_H of the blood towards the acid side. The administration of carbohydrate frees the body from an excess of acids by completing the combustion of the ketone substances. Chemical Abstracts.

Lead. IX. Solubility of Various Lead Compounds in Blood-serum. L. T. Fairhall (*J. Biol. Chem.*, 1924, **60**, 481—484).—Determinations have been made of the solubilities of various lead compounds in blood-serum at 25°. Whilst the values obtained for lead salts (carbonate 0·0333, sulphate 0·0437 g.p.l.) do not differ greatly from the corresponding solubilities in water, that for lead monoxide is distinctly greater (1·1520 g.p.l. against 0·0171 g.p.l. in water at 20°). Metallic lead has a solubility in blood-serum of 0·578 g.p.l. at 25°. Saturation of the serum with carbon dioxide decreased the value for lead to 0·1930, but produced no marked effect on the other solubilities. The results are of significance as indicating the ease with which lead oxides can enter the circulation from the respiratory tract. E. S.

Effect of Ultra-violet Light on the Condition of Calcium in the Blood. J. H. Clark (*Amer. J. Hyg.*, 1923, **3**, 481—482).—The diffusible calcium of blood-serum, measured by dialysis in collodion sacs against physiological saline, was found to be higher after the serum was exposed to radiation of a quartz-mercury arc. The diffusible calcium in rabbit-serum rose from 38 to 58%, in dog-serum from 44 to 53%. Chemical Abstracts.

Creatinine in the Blood. P. Fonteyne and P. Inglebrecht (*Ann. med.*, 1923, **14**, 470).—The creatine and creatinine content of the blood was determined in 100 healthy and sick subjects. The coefficient of secretion of creatinine remains longer intact than Ambard's ureosecretory coefficient. The amount of creatinine in the blood is comparatively independent of the diet.
Chemical Abstracts.

Chemistry of the Blood during Pregnancy. H. J. Stander (*Bull. Johns Hopkins Hosp.*, 1924, **35**, 133—137).—In non-pregnancy and pregnancy, respectively, 100 c.c. of blood contained, in mg.: non-protein nitrogen, 32, 28; urea nitrogen, 18·5, 12·48; uric acid, 3·3, 3·3; carbon dioxide combining power of plasma, 52, 44·5; ratio of urea nitrogen to non-protein nitrogen, 57, 44·5.
Chemical Abstracts.

Enzyme Content of the Blood. II. Variations in the Catalase and Protease Figures during 24 Hours in Animals and Man. E. Ivanitzky-Vassilenko and A. Bach (*Biochem. Z.*, 1924, **148**, 469—473).—Extreme daily variations in the blood catalase values are: in rabbits +33%, −10%; in cats +18%, −10%; in man +9%, −9% of the mean values in each case. The protease content shows wide variations up to ±100% of the mean. J. P.

Enzyme Content of the Blood. III. Catalase Values of the Blood of Thyroidectomised Goats. A. Bach and E. Cheraskova (*Biochem. Z.*, 1924, **148**, 474—475).—Thyroidectomy has no influence on the mean blood catalase value in goats.
J. P.

Eosinophile Granule Substance of the Blood and its Preparation, Nature, and Properties. I. Technique of Isolation. A. Neumann (*Biochem. Z.*, 1924, **148**, 524—528).—The isolation of the eosinophile granule substance from horse-blood fibrin is described. This substance is characterised by an intense benzidine peroxydase reaction and is very resistant to the action of acids and alkalis. J. P.

Animal Calorimetry. XXV. Relative Specific Dynamic Action of Various Proteins. D. Rapport [with J. Evenden] (*J. Biol. Chem.*, 1924, **60**, 497—511).—The specific dynamic action of a number of proteins (beef, casein, gliadin, codfish, chicken, gelatin) has been found to be approximately the same despite the large differences in their amino-acid composition. The addition of cystine to gelatin, which, it was considered, might lead to the production of glutathione in the organism, did not increase the specific dynamic action of this protein. E. S.

Animal Calorimetry. XXVI. Inter-relations between certain Amino-acids and Proteins with Reference to their Specific Dynamic Action. R. Weiss and D. Rapport [with J. Evenden] (*J. Biol. Chem.*, 1924, **60**, 513—544).—Although the specific dynamic actions of glycine and alanine, when administered simultaneously to a dog, are largely additive, the administration of glycine or alanine either orally, subcutaneously, or intravenously, simultaneously with the oral administration of protein (gelatin, casein), does not lead to a summation of effect unless the protein is fed in an amount which is small relative to the amount of amino-acid administered. The protein is apparently able to "neutralise" the action of the amino-acid. The specific dynamic actions of proteins, when fed together, are, however, additive. The authors consider it probable that certain amino-acids or polypeptides derived from the proteins combine with the glycine and so neutralise its specific dynamic effect. E. S.

Animal Calorimetry. XXVII. Administration of Various Proteins with Benzoic Acid to a Pig. F. A. Csonka (*J. Biol. Chem.*, 1924, **60**, 545—582).—When benzoic acid is included in the diet of a pig, it is eliminated in the urine in the form of hippuric acid, benzoylglycuronic acid (cf. Magnus-Levy, A., 1907, ii, 979), and free benzoic acid. The relative amounts of the two former substances excreted depend on the quantity of preformed glycine (free amino-acid or combined as protein) ingested. An increase in the latter. eads to an increase in the excretion of hippuric acid and a decrease in that of benzoylglycuronic acid. Hence the equality in the specific dynamic actions of equal amounts of different proteins with varying contents of glycine (cf. preceding abstracts) does not depend on the synthesis of this amino-acid in the organism. E. S.

Animal Calorimetry. XXVIII. Respiratory Metabolism of a Young Pig as Influenced by Food and Benzoic Acid. D. Rapport, R. Weiss, and F. A. Csonka [with J. Evenden] (*J. Biol. Chem.*, 1924, **60**, 583—601).—No definite effect on the heat production of the pig is produced by the ingestion, under varied dietary conditions, of benzoic acid (hence by the synthesis of hippuric acid) or of hippuric acid. Following a starchy meal, the conversion, by the pig, of carbohydrate into fat (cf. Lusk, A., 1915, i, 614) may continue for more than 21 hours; the maximum conversion observed amounted to 77% of that theoretically possible. E. S.

Metabolism of some Pyrimidines. H. J. Deuel, jun. (*J. Biol. Chem.*, 1924, **60**, 749—763).—No pyrimidines are excreted in normal urine. When fed to dogs in single doses of 1 to 3 g., thymine and uracil are partly metabolised (as shown by the rise, which usually occurs, in urinary carbamide) and partly excreted unchanged, but when the same amounts are administered in small doses they are completely destroyed in the organism. Following the ingestion of 50 g. of thymus-nucleic acid, the urine of a dog gave qualitative tests for pyrimidines. These results suggest that, contrary to current views, the destruction of pyrimidines contained in nucleic acid takes place after liberation from the latter. E. S.

Inorganic Metabolism. III. Significance of Phosphates in the Production of Tetany. F. P. UNDERHILL, E. G. GROSS, and W. COHEN (*J. Metab. Res.*, 1923, **3**, 679—709; cf. this vol., i, 452, 453).—Intravenous or intraperitoneal injection of sodium or potassium phosphate causes, with dogs and rabbits, a corresponding diminution of calcium. The intravenous administration of sodium hydrogen carbonate also produces tetany, but no diminution of calcium. The amount of calcium in the bones of rabbits is not affected by intravenous injection of comparatively large quantities of sodium orthophosphate. CHEMICAL ABSTRACTS.

Rate of Sugar Absorption in the Newborn. R. G. FLOOD (*J. Amer. Med. Assoc.*, 1924, **82**, 1595—1596).—The various sugars have different rates of absorption, dextrose being the most readily absorbed. The disaccharides show some of the characteristics of their component monosaccharides. Sucrose is not readily absorbed by very young infants, but the ability to utilise this sugar increases with the age of the infant. CHEMICAL ABSTRACTS.

Extraction and Precipitation of Soluble Proteins of Muscle. P. E. HOWE (*J. Biol. Chem.*, 1924, **61**, 493—522).—The concentration of a salt necessary for its maximum solvent action on muscle proteins has been shown to bear a definite relationship to the concentration of the same salt which will bring about precipitation of the blood proteins. When the solvent action of salt solutions towards muscle proteins was tested over a continuous range of varying concentrations, there were observed, for any one salt, certain zones of concentration in which the amount extracted was the same; these zones were taken to represent individual protein fractions. A method, based on this hypothesis, has been developed, whereby, using as solvent different molecular concentrations of a solution containing mono- and di-potassium phosphates in the ratio 1 : 2, it is possible to separate the proteins of muscle into six fractions. The work of Halliburton (A., 1887, 984) and of von Fürth (A., 1896, ii, 48) is reviewed in the light of this new fractionation, and details are given of the results of the method when applied to the muscles of various animals. C. R. H.

Creatine Content of Frog's Muscle during Work. I. H. SCHLOSSMANN (*Z. physiol. Chem.*, 1924, **139**, 87—94).—Stimulation of frog's muscle perfused with Ringer solution with or without the addition of creatine produces an increase in the creatine content of the muscle in the case of winter frogs but not in that of summer frogs. This corresponds with the smaller creatine content of the muscles of the former; stimulation evidently causes it to approach that of the latter. E. S.

Animal Nutrition. IV. Nitrogen, Ash, and Phosphorus Distribution in Beef Flesh. W. S. Ritchie, C. R. Moulton, P. F. Trowbridge, and L. D. Haigh (*Univ. Missouri Agr. Exp. Sta. Res. Bull.*, 1923, **59**, 1—78).—The ash of the fat of the rib is higher than that of the lean; total phosphorus is much higher in lean flesh than in fat. The ratio of soluble to total phosphorus increases as the animal grows thinner. The effects of age and of the plane of nutrition are investigated. Chemical Abstracts.

Photochemistry of the Visual Purple. S. Hecht (*J. Gen. Physiol.*, 1924, **6**, 731—740).—The velocity of bleaching of visual purple by light, under comparable conditions of concentration, volume, and surface exposed, is directly proportional to the intensity. D. R. N.

Aminogenesis in the Grey and White Substances of the Brain during Hunger. A. Palladin and D. Zuwerkalow (*Z. physiol. Chem.*, 1924, **139**, 57—63).—During fasting in dogs, the coefficient of aminogenesis—*i.e.*, the amino-acid nitrogen expressed as a percentage of the total nitrogen—of the grey substance of the brain is depressed and that of the white substance increased. E. S.

Chemistry of Bull's Testicles (Extractives). L. Leibfreid (*Z. physiol. Chem.*, 1924, **139**, 82—86).—αα-Dimethylguanidine has been isolated in the form of its chloroaurate, which was identical with that prepared by Schenck (A., 1912, i, 424). E. S.

Uric Acid Content of Human Amniotic Fluid. J. L. Williams and J. A. Bargen (*Amer. J. Obst. Gyn.*, 1924, **7**, 406).—Uric acid and creatinine are present in human amniotic fluid in greater concentration than in blood. The amounts of carbamide, non-protein nitrogen, and uric acid in the fluid increase as the term of pregnancy is prolonged. Chemical Abstracts.

Spinal Fluid Sugar. B. J. Alpers, C. J. Campbell, and A. M. Prentiss (*Arch. Neurol. Psychiatry*, 1924, **11**, 653—663).—The spinal fluid dextrose normally varies from 50 to 84 mg. per 100 c.c.; average figures are given for various pathological conditions. Chemical Abstracts.

Natural Porphyrins. XI. H. Fischer, H. Kämmerer, and A. Kühner (*Z. physiol. Chem.*, 1924, **139**, 107—117).—The sterile autolysis of beef always gives rise to Kämmerer's porphyrin, which can be demonstrated spectroscopically after about 10 days; after 6 weeks the spectrum of coproporphyrin can also be observed. These results are similar to those previously obtained in the putrefaction of meat (this vol., i, 894). C. R. H.

Hydrogen-ion Concentration of the Cerebro-spinal Fluid of Children. K. Waltner (*Biochem. Z.*, 1924, **149**, 145—149).—The p_H of the cerebro-spinal fluid from normal children is 7·50 to 7·55; in tuberculous meningitis it is unchanged, whilst in purulent meningitis it may be somewhat lower. Successive fractions taken during a lumbar puncture tend to become more acidic. J. P.

Comparison of the Metabolism of some Mineral Constituents of Cow's Milk and of Human Milk. C. C. WANG and L. H. DAVIS (*Amer. J. Diseases Children,* 1924, **27**, 569—577; cf. *ibid.*, 352).—The greater intake of chlorine with cow's milk causes an increase in the excretion of chlorine. The utilisation of chlorine runs parallel to the urinary chlorine; there is no marked difference in percentage utilisation of chlorine intake between the two milks. As age increases there is a decrease in the amount of chlorine retained with cow's milk, but not with human milk.
CHEMICAL ABSTRACTS.

Reaction of the Urine of the Horse. F. PÁDÁR (*Biochem. Z.*, 1924, **149**, 200—205).—Electrometric determinations of the influence of varying carbon dioxide tensions on the reaction of horse's urine show that it behaves like a bicarbonate solution, low carbon dioxide tensions producing a much steeper relative fall in the curve of hydroxyl-ion concentration than do higher tensions.
J. P.

Gastric Secretion and the "Alkaline Tide" in Urine. R. S. HUBBARD, S. A. MUNFORD, and E. G. ALLEN (*Amer. J. Physiol.*, 1924, **68**, 207—212).—The alkaline tide was absent in the urine of individuals whose gastric juice did not contain hydrochloric acid.
A. A. E.

Uric Acid Excretion. A. E. KOEHLER (*J. Biol. Chem.*, 1924, **60**, 721—736).—Ingestion of uric acid does not appreciably raise the level of uric acid in the blood nor does it increase its excretion in the urine. After intravenous injection approximately 50% may be recovered from the urine. The amount of uric acid retained in the blood 2 hours after injection and its rate of excretion may serve as guides in determining renal insufficiency. E. S.

Origin of Urinary Ammonia. R. F. LOEB, D. W. ATCHLEY, and E. M. BENEDICT (*J. Biol. Chem.*, 1924, **60**, 491—495).—That the ammonia content of the renal venous blood of the dog is much greater than that of arterial blood (Nash and Benedict, A., 1922, i, 191) has been confirmed and it has been further found that venous blood from other sources has an ammonia content slightly greater than that of arterial blood. With an animal (rabbit) which does not excrete appreciable amounts of ammonia in the urine the ammonia content of the renal venous blood is practically identical with that of arterial blood. These results give further support to the theory of Nash and Benedict that the kidney is the seat of formation of urinary ammonia. E. S.

Variations in Rate of Excretion of Acetone Compounds. R. S. HUBBARD and F. R. WRIGHT (*J. Biol. Chem.*, 1924, **61**, 377—385).—Subjects fed on diets of which the ketogenic ratio (cf. Shaffer, A., 1922, i, 83) was between 1 : 1 and 2 : 1 showed an increased excretion of acetone compounds, although not so much as is required by the theory that 1 mol. of antiketogenic material can bring about the combustion of only 1 mol. of ketogenic material. The rate of excretion showed considerable diurnal variations, being usually at its height soon after food and not running parallel with the rate of excretion of urine. C. R. H.

Ether Anæsthesia. III. Rôle of Lactic Acid in the Acidosis of Ether Anæsthesia. E. Ronzoni, I. Koechig, and E. P. Eaton (*J. Biol. Chem.*, 1924, **61**, 465—492).—The acidosis observed in ether anæsthesia appears, from a series of experiments on dogs, to be chiefly due to the accumulation of lactic acid derived from the tissues; in view of the loss of phosphate from the muscles during anæsthesia observed by Stehle and Bourne (this vol., i, 900), this may indicate a breakdown in the muscle of a hexosephosphate such as the lactacidogen of Embden (A., 1921, i, 528). The view of Anrep and Cannan (*J. Physiol.*, 1923—24, **58**, 244) that accumulation of lactic acid is controlled by the p_H of the blood through the tension of carbon dioxide, is not supported by the experiments.
C. R. H.

Excretion of Phosphoric Acid during Anæsthesia. W. Bourne and R. L. Stehle (*J. Amer. Med. Assoc.*, 1924, **83**, 117—118; cf. A., 1922, i, 1085, and *J. Biol. Chem.*, 1924, **60**, 17).—Eleven of fifteen cases of surgical anæsthesia showed in consequence a definitely increased excretion of phosphorus. The effect is usually most pronounced during the anæsthesia, but with chloroform, and with ether preceded by morphine, it is later. The chloride excretion does not show any significant variations. Apparently phosphoric acid is responsible for the acidosis of anæsthesia.
Chemical Abstracts.

Low Nitrogen Metabolism with Low Carbohydrate Diet in Diabetes. K. Petren (*J. Biol. Chem.*, 1924, **61**, 355—363).—The total nitrogen metabolised, as indicated by the ratio, grams total urinary nitrogen : kg. body-weight, may be maintained at a very low level for prolonged periods in diabetics receiving a diet poor in protein and carbohydrate but rich in fat; this indicates that the sparing effect of fat ingestion on nitrogenous metabolism is greater than has hitherto been supposed. C. R. H.

Lipæmia. I. Micro-determination of Blood Fat. H. I. Bing and H. Heckscher (*Biochem. Z.*, 1924, **149**, 79—82).—The blood is absorbed on filter-paper, extracted by a suitable fat solvent, and the turbidity of a solution of the fat in 99·5% alcohol, after treatment with an aqueous solution of 1% barium chloride, is compared with standard opacity suspensions in a Heckscher nephelometer (*Compt. rend. Soc. Biol.*, 1921, **85**, 378). J. P.

Lipæmia. II. Blood Fat in Normal Human Subjects. H. I. Bing and H. Heckscher (*Biochem. Z.*, 1924, **149**, 83—89).—In 155 cases out of 213 examined, the fat content of the normal blood in a fasting condition lay between 0·05% and 0·13%. The remaining 58 cases showed values between 0·14% and 3·16%. The incidence shows a maximum at 0·10%. The individual fasting blood-fat value remains practically constant. The blood fat reaches a maximum in from 3 to 5 hours after a meal, but the form of the blood-fat curve varies with the nature of the diet. Direct observation of the turbidity of the blood-serum is not a trustworthy indication of the fat content. J. P.

Lipæmia. III. Pathological Changes in the Blood-fat Value. H. I. Bing and H. Heckscher (*Biochem. Z.*, 1924, **149**, 90—99).—Children and young people often have blood-fat values below normal. Hypolipæmia was found in three cases of Basedow's disease, hyperlipæmia in cases of acute lung and uncompensated heart affections, in cases of icterus, in various types of nephritis, in diabetes mellitus, and in cases of disturbed endocrine function involving fat metabolism. In some cases the hyperlipæmia was latent, *e.g.*, in arthritis urica the fasting value was normal and the abnormality was revealed only after a meal. J. P.

Amino-acids in Physiological Fluids. G. Wolpe (*Münch. med. Woch.*, 1924, **71**, 363—365; from *Chem. Zentr.*, 1924, i, 2377).—Increased amino-acid content in the blood-serum in malaria and leucæmia is due to increased decomposition of blood proteins. There appears to be a correlation between the resistance of the organism and the amino-acid content in physiological fluids. Amino-acid production may be connected with disturbances in the endocrine glands. G. W. R.

Relation of Acidosis and Hyperglycæmia to the Excretion of Acids, Bases, and Sugar in Uranium Nephritis. B. M. Hendrix and M. Bodansky (*J. Biol. Chem.*, 1924, **60**, 657—676).—The acidosis which, together with hyperglycæmia and glycosuria, is produced in dogs by administration of uranium acetate is accompanied in the early stages by an increased excretion of basic phosphates and salts of organic acids, and in the later stages by a marked decrease in phosphate excretion. No constant relationship appears to exist between the degree of acidosis and the hyperglycæmia and glycosuria. E. S.

Chemistry of Osteohæmochromatosis in Animals. D. von Deseö (*Biochem. Z.*, 1924, **149**, 191—199).—The pigment occurring in the bones of animals with osteohæmochromatosis has chemical and spectroscopic properties which suggest that it originates from blood pigment and is possibly a hæmatoporphyrin. J. P.

Rate of Excretion of Urea in the Toxæmias of Pregnancy. H. J. Stander, E. C. Duncan, and B. L. Moses (*Bull. Johns Hopkins Hosp.*, 1924, **35**, 97—103).—Average results are given for non-pregnant, pregnant, and pathological conditions.

Chemical Abstracts.

Excretion of Tryparsamide. A. G. Young and C. W. Muehlberger (*J. Pharm. Exp. Ther.*, 1924, **23**, 461—464).—At least part of the tryparsamide is excreted unchanged in the urine and in three out of four normal individuals 88—95% of the arsenic of the drug was excreted within the first 24 hours. Some individuals show a much slower rate of excretion, and may therefore be more susceptible to cumulative effects of the drug. D. R. N.

Test-tube Reaction for Damage and Death of Tissues. P. Rostock (*Fermentforsch.*, 1924, 8, 72—85).—After testing the various reactions which have been proposed for distinguishing between living and dead tissues, the author concludes that the most trustworthy are the dinitrobenzene reaction of Lipschitz (*Pflüger's Arch.*, **199**) and the nitroanthraquinone reaction of Bieling (*Zentr. Bakt.*, 1923, **90**). C. R. H.

Effect of Potassium on the Acid Metabolism of Surviving Skeletal and Cardiac Muscles of the Frog. F. R. Griffith (*J. Gen. Physiol.*, 1924, 6, 683—695).—The potassium contraction of skeletal muscle and relaxation of cardiac muscle have been correlated with the carbon dioxide and total acid production of these tissues. The immersion of surviving sartorius muscles of the frog in isotonic potassium chloride solution causes a marked increase in the rate of acid production, carbon dioxide being probably the principal acid involved. Surviving cardiac muscle treated in a similar manner shows a pronounced depression in the rate of acid production. It is believed that these changes in metabolism may be independent of the stimulation and inhibition of contraction which potassium simultaneously produces in these tissues.

D. R. N.

Factors influencing Chemical Processes of Fracture Healing. R. Schwarz, R. Eden, and E. Herrmann (*Biochem. Z.*, 1924, **149**, 100—108).—Ossification after fracture consists primarily in the addition of calcium to organic substances and the secondary combination of phosphoric acid with the fixed calcium until a ratio Ca : P=1 : 0·6 is attained, at which stage the cartilage becomes ossified. J. P.

Mechanism of Phloridzin Diabetes. T. P. Nash, jun., and S. R. Benedict (*J. Biol. Chem.*, 1924, **61**, 423—428).—The fact that insulin may be obtained by the usual procedure from the pancreas of phloridzinised dogs is evidence against the view of Ringer (this vol., i, 446) that the effect of phloridzin is to injure the pancreas, rendering it unable to produce insulin. C. R. H.

Action of Quinine on Protein Metabolism, Respiratory Exchange, and Heat Function. I. Protein Metabolism. S. W. Hardikar (*J. Pharm. Exp. Ther.*, 1924, **23**, 395—448).—The view generally held that quinine diminishes heat production by lowering nitrogen metabolism is not substantiated. Quinine has no influence on protein metabolism even in doses which may be toxic in themselves. D. R. N.

Pressor Anæsthetics. C. S. Marvel and V. du Vigneaud. (See i, 1193.)

Experiments with Anæsthetic Gases, Propylene, Methane, and Methyl Ether. W. E. BROWN (*J. Pharm. Exp. Ther.*, 1924, **23**, 485—496).—Propylene induces anæsthesia at a concentration as low as 37% when mixed with either oxygen or air. Anæsthesia may be maintained satisfactorily at a concentration as low as 20%. In concentrations of about 65% or higher it is poisonous. Methane produces anæsthesia only at high concentrations (87%) whilst 90% methane administered to a cat caused irregular respirations which gradually ceased. Methyl ether produces anæsthesia at concentrations of 65%; 85% causes profound anæsthesia with gradual cessation of respiration. D. R. N.

Chloroform Poisoning. H. J. STANDER (*Bull. Johns Hopkins Hosp.*, 1924, **35**, 46—49).—In a fatal case of delayed chloroform poisoning there was an increased output of urinary nitrogen with a marked decrease of the urea-nitrogen % and a steadily rising ammonia coefficient; a very definite drop in the carbon dioxide-combining power of the blood to 27·4 vols. %, an increase in the blood of non-protein nitrogen, urea, uric acid, and amino-acids, and a fall in blood-sugar to 0·058%. These changes indicate an increased destruction but incomplete oxidation of the proteins.
CHEMICAL ABSTRACTS.

Physiological Actions of Cyanides. T. H. BODINE (*J. Gen. Physiol.*, 1924, **7**, 19—23).—The physiological action of hydrocyanic acid and its salts depends on (*a*) the ease with which hydrogen cyanide penetrates living cells as such and then ionises; (*b*) the presence of large amounts of the free acid even in the presence of cyanides; (*c*) specific effects due to chemical activity. Hydrocyanic acid in acid, neutral, or slightly alkaline media produces intracellullar acidity on account of its rapid penetration into the cell. It acts specifically on certain protozoa, the resistance towards it being the reverse of that to mineral acids. O. O.

Toxicity of a Polymeride of Hydrocyanic Acid. CH. BEDEL (*J. Pharm. Chim.*, 1924, [vii], **30**, 189—193).—Dicyanomethylamine hydrocyanide, $[HCN]_4$, is much less toxic than hydrocyanic acid, the minimum lethal dose being about 0·75 g. per kg. body-weight when given by mouth. The symptoms of poisoning are similar to those of hydrocyanic acid, but sodium thiosulphate is without effect as an antidote. C. R. H.

Biochemistry of Carotinoid Pigments in Animals. L. S. PALMER (*Minnesota Agr. Exp. Sta., Ann. Rept.*, 1922, 43—44).—The yellow lipochrome of cod-liver oil is not a carotinoid and cannot be removed completely by treatment with charcoal. The yellow pigment in the blood serum of pigeons has been identified as xanthophyll. The red pigment in the feet and legs resembles carotin in its solubility, but not in other respects. Alcoholic solutions treated with lime-water yield an amorphous pigment, which gives a blue colour when treated with ferric chloride instead of a green, characteristic of carotin and xanthophyll. Human organisms lose carotinoid pigments by the process of oxidation.

Carotinoid skin colorations are due to lowered oxidation processes of the body and super-abundance of carotinoids in the diet.

CHEMICAL ABSTRACTS.

Concentration of Silver Ions in Solutions of Colloidal and Complex Silver Preparations with Special Reference to their Medicinal Use. H. SCHLEE (*Biochem. Z.*, 1924, **148**, 383—432).—Excess of sodium chloride in a solution of silver chloride diminishes the silver-ion concentration in accord with the solubility-product equation. Egg-albumin has a similar but more marked effect on solutions of silver nitrate, and this persists after the protein has been dialysed to remove naturally occurring sodium chloride. Blood-serum has a still more marked effect in diminishing the silver-ion concentration. The findings of Paul (*Z. Elektrochem.*, 1912, **18**, 521) with regard to the classification of medicinal silver preparations into three groups are confirmed. It is possible from such behaviour to draw conclusions as to the nature of the silver in these preparations. Determinations were made of the silver-ion concentration of the blood after injections of certain colloidal silver preparations.

J. P.

Photodynamic Phenomena. III. Fixation of Active Dyes in the Cell. P. METZNER (*Biochem. Z.*, 1924, **148**, 498—523).—Photodynamically active dyes show in general negative phototaxis. Cresyl fast violet exhibits induced photokinesis. In the cell, the active portion of the dye is adsorbed and shows absorption and fluorescent spectra which differ from those of the substance when in solution, being displaced towards the red. It is suggested that the active adsorbent is a phosphatide or a tyrosine compound. The activity spectra and absorption spectra are approximately proportional without showing exact correspondence, and the former is also displaced towards the red in the adsorbed dye. It is concluded that photodynamic dyes become active only within the cell.

J. P.

Permeability of Living and Dead Cells. III. Penetration of certain Alkalis and Ammonium Salts into Living and Dead Cells. M. M. BROOKS (*U.S. Pub. Health Rpts.*, 1923, **38**, 2074—2086, *Reprint No.* 866)—The rate of penetration of bases into living cells has been measured, using the marine alga, *Valonia ventricosa*, and the method previously described (cf. *ibid.*, 1923, **38**, 1449). Ammonia, ammonium chloride, sulphate, and carbonate cause an increase in the p_H of the sap of *Valonia*, due to the penetration of free ammonia. On removal of the ammonia by aëration, the p_H of the sap returns to normal. Both ions of ammonium carbonate penetrate and can be removed by aëration. Solutions of sodium and potassium hydroxides penetrate into the cell sap very much more slowly than an ammonia solution having the same p_H. Dead cells rapidly assume the p_H of the surrounding solution. The results confirm the view that the relative p_H of the sap of living cells and of the solution surrounding them is greatly influenced by the nature of the ions present in the solution.

C. T. G.

Permeability of Living and Dead Cells. IV. Penetration of Tervalent and Quinquevalent Arsenic into Living and Dead Cells. M. M. Brooks (*U.S. Pub. Health Rpts.*, 1923, **38**, 2951—2966, *Reprint No.* 888).—Determinations have been made of the amount of arsenic passing from surrounding solutions into the sap, protoplasm, and cell-wall of *Valonia* (cf. preceding abstract). Arsenic, whether in the quinquevalent form (as As_2O_5 and atoxyl) or in the tervalent form (as As_2O_3), penetrates least when the solution is nearly neutral. With increasing alkalinity or acidity more arsenic is taken up. Tervalent arsenic, from acid solutions, penetrates less readily into the protoplasm but more readily into the sap than quinquevalent arsenic; in alkaline solutions, the behaviour of the two forms is similar. Previous exposure of the cells in sodium hydrogen carbonate solution (when carbon dioxide accumulates in the sap) increases by 150% the quiquevalent arsenic and reduces by 25% the tervalent arsenic taken up by protoplasm; on the other hand, the tervalent arsenic taken up by the sap is increased by about 100% and the quinquevalent arsenic only by about 25%. Penetration of arsenic into dead cells is much more rapid than into living cells. The use of phosphate buffer solutions to maintain a constant p_H sometimes led to untrustworthy results.

C. T. G.

Formation of Pigment. I. Enzymic Pigment Formation as an Aid to Classification. H. Schmalfuss (*Fermentforsch.*, 1924, **8**, 1—41, 86—115). **Formation of Pigment. II.** H. Schmalfuss and F. Werner (*ibid.*, 116—134).—The formation of pigment from *l*-α-amino-β-3 : 4-dihydroxyphenylpropionic acid (called for brevity the " D-reaction ") by an enzyme from caterpillar's blood, is increased by the presence of oxygen; nitrogen, hydrogen, acetylene, carbon monoxide and dioxide, and nitrous oxide are indifferent, whilst sulphur dioxide, hydrogen sulphide, hydrocyanic acid, cyanogen, chlorine, bromine, and ammonia inhibit the reaction. The effect of other organic substances, both alone and in presence of " D," on pigment formation by this enzyme was tested in a large number of cases. The substances investigated fell into four groups, according to whether or not they inhibited the formation of pigment from " D," and whether or not they could themselves act as precursors of pigment. The application of these criteria made it possible in many instances to distinguish between isomerides, *e.g.*, between *o*-, *m*-, and *p*-cresol. Formation of melanin could be demonstrated when strips of filter-paper, previously treated with a solution of egg-albumin in strong potassium hydroxide, were immersed in solution either of " D " or of pyrocatechol.

The above experiments were extended to enzyme preparations derived from the body fluids of a number of different animal species; by the application of the same criteria a series of results was obtained which, it is claimed, may form a useful support to morphological grounds of classification.

Although in the case of the precursor " D " the formation of pigment by the enzyme from caterpillar's blood is very much accelerated by oxygen, the effect of the latter with other precursors is less marked. The reaction does not take place in anhydrous solvents and is not affected by light. The effect of heat shows that two active agents are involved, one heat-labile, which reaches its optimum at 40° and is inactivated at 70°, and the other heat-stable, which increases in activity up to 100°. The enzyme is destroyed by acids and inhibited by bases. Preparations from caterpillar's blood become more active with keeping, both as regards catalase and oxydase, but both fresh and old preparations are destroyed with equal ease by dilute sulphuric acid. C. R. H.

Investigation of Amylase. P. Rona and C. van Eweyk (*Biochem. Z.*, 1924, **149**, 174—187).—A method for investigating amylolytic activity is described in which glycogen is used as the substrate, its concentration being determined continuously throughout the course of the reaction by means of the nephelometer. J. P.

Amylase. K. Sjöberg and E. Eriksson (*Z. physiol. Chem.*, 1924, **139**, 118—139).—Amylase from barley after germination can carry the hydrolysis of starch further than that obtained before germination; with the most active amylase, however, there could not be obtained a greater yield of maltose than 80%. Separate experiments with amylose and amylopectin as substrates showed that these substances individually were hydrolysed to the extent of 80% also. The affinities of the enzyme for amylose and amylopectin are of the same order of magnitude, but not identical. The inhibiting effects of maltose and dextrose are different according to whether they are measured by the rate of maltose production or by the rate of disappearance of the iodine reaction. This supports the hypothesis that two enzymes are concerned in the hydrolysis of starch by amylase. C. R. H.

Antiamylase. H. Lüers and F. Albrecht (*Fermentforsch.*, 1924, **8**, 52—72).—The serum of rabbits which have been injected subcutaneously with preparations of amylase contains a substance which inhibits the action of the enzyme; such serum also gives a precipitin reaction with solutions of the amylase injected. These reactions are in a high degree specific to the particular amylase employed. The anti-body to the enzyme is stable when heated at 56°. After the injection of amylase, previously inactivated by heat, the precipitin reaction is still obtained, but the serum has no inhibitory action towards the enzyme. There are therefore involved two distinct immunity reactions, the production of an anti-body to the enzyme itself, and of another to the protein which accompanies it. C. R. H.

Relation between Catalase and Autoxidisable Substances. D. Rywosch (*Fermentforsch.*, 1924, **8**, 48—51).—The presence of catalase in the body fluids of invertebrates has been demonstrated to run parallel with the presence therein of an autoxidisable chromogen. C. R. H.

Stability of Yeast Catalase. K. Nakamura (*Z. physiol. Chem.*, 1924, **139**, 140—146).—The observed rate of inactivation of yeast catalase during autolysis of yeast is about 20,000 times greater than can be accounted for by the effect of temperature alone; this is apparently due to the presence of enzymes which destroy catalase. C. R. H.

Rôle of the Mineral Constituents in Plants. I. Influence of Neutral Salts on Catalase. A. J. SMIRNOV and S. P. ALISSOVA (*Biochem. Z.*, 1924, **149**, 63—78).—The reaction of aqueous extracts of wheat containing naturally occurring buffer salts is not altered by the addition of the chlorides of univalent metals, whilst the chlorides of the bivalent metals lower the $p_{\rm H}$ by 0·2 to 0·6. By increasing the $p_{\rm H}$ from 3·5 to 7·3, the relative activity of the catalase present increases from 4·76 to 135·98. Bivalent cations inhibit the activity of catalase twice as strongly as univalent cations, whilst a similar relation between inhibitory power and valency is not observed in the case of the anions, the series being $SO_4 < PO_4 < Cl < NO_3$ in the order of increasing inhibition. Univalent cations are active in concentrations of *M*/320, bivalent cations at *M*/640. At still greater dilutions down to *M*/5120, a zone of very weak or of no inhibition is followed by one at which the inhibition again appears. J. P.

Influence of Culture of Yeast on Galactose on its Power of Fermenting this Carbohydrate. E. ABDERHALDEN (*Fermentforsch.*, 1924, **8**, 42—47).—The fact, previously recorded by other observers, that yeast, grown in a medium containing galactose, acquires an increased power of fermenting this carbohydrate, has been confirmed; similar results were obtained with the maceration juice of yeast so treated. No evidence could be obtained of increased permeability of the yeast-cells to galactose. It is suggested that, prior to fermentation, galactose must be transformed into dextrose or lævulose, and that suitable conditions for such a transformation are established in the cells by the presence of galactose in the culture medium. C. R. H.

Fermentation Co-enzyme (Co-zymase) of Yeast. V. The Rôle of the Co-enzyme in Fermentation. H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **139**, 15—23).—A parallelism, which is not disturbed by variations in the co-enzyme content of the yeast, has been found to exist between the evolution of carbon dioxide and the esterification of phosphates during the fermentation of dextrose by yeast. It is concluded that the co-enzyme takes part in the formation of the hexosediphosphate or perhaps in an earlier transformation of the sugar. E. S.

Dependence of Alcoholic Fermentation on Acidity. K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **139**, 30—38).—A comparison has been made between the conditions of activity of a bottom yeast, with which esterification of phosphates (decrease of free phosphates) accompanied fermentation, and a top yeast, which produced no detectable decrease in free phosphates; dry preparations were used in each case. No essential difference was found between the velocity–$p_{\rm H}$ curves. From this result, together with the effect of phosphates on the course of the fermentation, it is concluded that the two yeasts differ only in the rate at which they decompose hexosephosphates; this rate is small with the bottom yeast and hence an accumulation of hexosephosphates occurs. E. S.

Rotation of the Maltose produced by Fermentation of Starch by Malt Extract. H. VON EULER and K. HELLEBERG (*Z. physiol. Chem.*, 1924, **139**, 24—29).—Preliminary experiments indicate that the maltose so produced contains a preponderating amount of the β-form. E. S.

Enzymic Methylglucoside Equilibrium. H. VON EULER and K. JOSEPHSON (*Arkiv Kem., Min., Geol.*, 1924, **9**, No. 7, 1—8).—For the reversible enzymic hydrolysis of β-methylglucoside, represented by the equation [β-methylglucoside–enzyme]+[water] $\rightleftharpoons$ [glucose–enzyme]+[methyl alcohol], there exist the equilibria [methylglucoside–enzyme]/[methylglucoside] . [enzyme]$=K_1$ and [glucose–enzyme]/[glucose] . [enzyme]$=K_2$. The velocity equations are, for the hydrolysis of the glucoside, $v_1=k_1$[glucoside–enzyme] . [water] and for the synthesis, $v_2=k_2$[glucose–enzyme] . [alcohol]. The progress of the reaction in the system, glucoside–glucose–alcohol–water–enzyme is hence determined by the expression, $dx/dt=v_1-v_2=k_1$[glucoside–enzyme] . [water]$-k_2$[glucose–enzyme] . [alcohol]$=k_1K_1$[glucoside] . [enzyme] . [water]$-k_2K_2$[glucose] . [enzyme] . [alcohol]. For a condition of equilibrium, $dx/dt=0$, and hence

$$k_1/k_2=K_2[\text{glucose}]\,.\,[\text{alcohol}]/K_1[\text{glucoside}]\,.\,[\text{water}]=K.$$

Only when $K_1=K_2$ can the position of equilibrium in this system coincide with that in the corresponding non-enzymic system.

Bourquelot (*J. Pharm. Chim.*, 1914, [vii], **10**, 361) has shown that the same equilibrium position is arrived at in the hydrolysis as in the synthesis of β-methylglucoside in presence of emulsin. By means of Bourquelot's results, the authors show that the value of K_1 in the expression, [methyl alcohol][glucose]$=K_1$[water][glucoside] remains practically constant at 0·25 for concentrations of the alcohol not exceeding about 50% and afterwards gradually rises, probably owing to increasing inactivation of the enzyme, this altering the final state and resulting in a false equilibrium. Thus, according to the theory outlined above, the affinity of β-glucosidase for glucose is about four times as great as that for methylglucoside, whereas the value of the equilibrium constant derived from the velocities of the two reactions should be 1. The affinities between the β-methylglucosidase used by Bourquelot and the reacting substances are not known, but for the emulsin employed by Willstätter, Kuhn, and Sobotka (A., 1923, i, 1034; see also Kuhn, A., 1923, i, 589; Willstätter and Kuhn, A., 1923, i, 721), the ratio between such affinities is calculated to be 3·3, which differs but little from the value 4 for the different preparation of enzyme used by Bourquelot. T. H. P.

Blood Diastases. I. S. J. COHEN (*Amer. J. Physiol.*, 1924, 69, 125—131).—Since hyperglycæmia produced by adrenaline or morphine, but not by ingestion of carbohydrate, and hypoglycæmia produced by insulin are associated with a fall in the blood diastase and an increase in the liver-tissue diastase, it is suggested that the function of the blood diastases is to assist in the breaking down of glycogen, and to be available for mobilisation to the organs where there is immediate need for their action. A. A. E.

Enzyme Action. XXVIII. Spontaneous Increase in the Activities of Lipase and Protease of Tissue Extracts. (Miss) H. M. Noyes, K. Sugiura, and K. G. Falk (*J. Amer. Chem. Soc.*, 1924, **46**, 1885—1889; cf. A., 1923, i, 872).—The tissues investigated were whole rats (3½ and 22 days old), rabbit liver, lung, and muscle, mouse carcinoma, and human fibromyoma of uterus. They were ground up, extracted with water, and the filtered extracts tested for lipase and protease immediately and at intervals after standing at the ordinary temperature in the presence of toluene. The lipase was determined by adding 3·4 milli-equivalents of ten different esters to 15 c.c. portions of the extracts, incubating at 37° for 22 hours, and then titrating with 0·1*N*-sodium hydroxide. For the protease actions, 0·1 g. portions of peptone, casein, and gelatin were added to the extracts to be tested and titrated by the formol method after similar incubation. The mixtures were all brought to p_H 7·0 initially. In the lipase experiments spontaneous increases were observed with some tissues and substrates and not with others. Spontaneous increases in protease action usually occurred with casein, and not with the other two substrates. A. C.

Application of Folin's Method for the Determination of Amino-nitrogen to Peptic Digestion. Y. Uwatoko (*Z. physiol. Chem.*, 1924, **139**, 76—81).—No increase in amino-acid nitrogen occurs during the digestion of casein or glycine anhydride with pepsin. Some ammonia is produced from the casein, but this is also formed by treatment with 1% hydrochloric acid at 37° alone.

E. S.

Kinetics of Trypsin Digestion. J. H. Northrop (*J. Gen. Physiol.*, 1924, **6**, 723—729).—The rate of digestion of concentrated casein solutions with small amounts of trypsin has been followed with a view to prove the validity or otherwise of Schütz's rule, according to which the amount of hydrolysis should be proportional to the square root of the product of the time into the enzyme concentration. Neither Schutz's rule nor Arrhenius' equation holds accurately owing to the incorrectly assumed relation between the rate of hydrolysis and the substrate concentration.

D. R. N.

Enzymic Action of Extracts of the Duodenal Region of Domestic Animals. H. D. Bergman, H. H. Dukes, and J. H. Yarborough (*J. Amer. Vet. Med. Assoc.*, 1924, **65**, 313—326).—Extracts were made from the duodenal substance of the horse, ox, sheep, and pig. The extracts invariably contained an amylolytic enzyme active in neutral solution. This action was greater than that of extracts of the submucosa of these regions, leading to the belief that the duodenal cells themselves produce amylase. Protease and lipase were generally not found.

CHEMICAL ABSTRACTS.

Nucleosidases. I. General Properties. P. A. LEVENE, M. YAMAGAWA, and I. WEBER (*J. Biol. Chem.*, 1924, **60**, 693—706).—The kinetics of the decomposition of adenosine by nucleosidase have been investigated. Solid preparations of the enzyme were obtained by extracting the minced organs (spleen, kidney) with a phosphate buffer solution (p_H 7·0) and pouring the press-juice, after concentration, into a large volume of acetone. These, however, rapidly lost their activity; hence the press-juice was mostly employed without further purification. The optimum conditions for the action of nucleosidase are at p_H 7·5 and 37°, although irreversible inactivation occurs at much lower temperatures. With a relatively large excess of enzyme, the reaction follows the unimolecular law; deviations from this law are considered to be due to the formation of the complex enzyme–inhibitor, but attempts to calculate the dissociation constant of the latter yielded values which differed with different enzyme preparations. Both products of the reaction (adenine, ribose) exert an inhibitory action; the effect of ribose is twice that of adenine.

E. S.

Nucleosidases. II. Purification of the Enzyme. P. A. LEVENE and I. WEBER (*J. Biol. Chem.*, 1924, **60**, 707—715).—The nucleosidase was extracted by suspending the washed and ground organs (2·2 kg.) in a phosphate buffer solution (4 litres) at p_H 7·0, allowing them to autolyse for 24 hours at 40°, and filtering. When kidneys were employed, the activity of the extract was increased by digesting the filtrate for a further 24 hours at 40°; with pancreas this further digestion produced inactivation. Purification was effected by fractional precipitation with colloidal iron and alcohol. Addition of 20% (by volume) of iron solution and 20% of alcohol removed the inhibitory substances; the further addition to the filtrate of 40% of iron solution and 40% of alcohol (95%) completely precipitated the enzyme. The latter was extracted from the adsorbate by disodium phosphate or sodium hydroxide at p_H 8·7. After filtration from the iron, the extract was neutralised, concentrated under diminished pressure, and the enzyme precipitated by a large excess of acetone. The solid preparation so obtained retained its activity for 10 months. It contained large amounts of inorganic material (76% ash) which could not be removed by dialysis without disappearance of the enzyme. Further purification could sometimes be effected by bringing a solution of this preparation to p_H 1·2 by addition of hydrochloric acid, when a highly active product separated as a flocculent precipitate (ash 8%); this method was not, however, invariably successful. The most active preparation gave a pink biuret reaction, but no distinct reaction with Millon's reagent; it did not reduce Fehling's solution. Nucleosidase is adsorbed by kaolin, but not by aluminium hydroxide; in the former case, the adsorbate possesses the whole of the original activity, but the enzyme cannot be recovered.

E. S.

Nucleosidases. III. Degree of Specificity of Nucleosidase and Distribution of it in Various Organs and in Various Species. P. A. Levene and I. Weber (*J. Biol. Chem.*, 1924, **60**, 717—720).—The optimum acidity for the decomposition of inosin by nucleosidase is identical with that for adenosine (cf. preceding abstracts). Nucleosidase is absent from dog's pancreas and from pancreatic and intestinal juices, but is present in the pancreas of cattle. It has no action on adenine hexoside.

E. S.

Action of Antiphenolase in an Adsorbed Condition. W. Engelhardt (*Biochem. Z.*, 1924, **148**, 463—468).—Antiphenolase, together with the serum proteins, is adsorbed from immune sera by ferric and aluminium hydroxides, charcoal, and kaolin. The adsorption is practically irreversible, and the adsorbed enzyme retains undiminished its specific affinity for phenolase in the cases of the first three adsorbents, whilst its activity is but slightly diminished in the case of kaolin. J. P.

Coagulating Property of Papain. L. Rosenfeld (*Biochem. Z.*, 1924, **149**, 158—173).—Papain solution precipitates an aqueous solution of the mucilage prepared from the seeds of *Cydonia*. Pepsin, trypsin, rennin, and plant protease do not precipitate the mucilage. The specific affinity of papain for *Cydonia* mucilage is such that the latter may be identified and separated from mixtures with other similar substances. *Cydonia* mucilage carries a negative charge whilst papain is positive. The precipitation is therefore explained on physical grounds. The precipitate consists of both constituents and separation is difficult, although the precipitated enzyme is still capable of coagulating milk. Alkalis, inorganic acids, neutral salts, and the globulin of blood-serum inhibit the action of papain, whilst organic acids have the opposite effect. Papain also coagulates agar-agar. J. P.

Milk-coagulating Enzyme of *Solanum elæagnifolium*. A. Bodansky (*J. Biol. Chem.*, 1924, **61**, 365—375).—The chymase obtained from the berries of the above plant acts best at 80—85° and is more stable to heat than rennin from animal sources; the preparation showed no change in activity after dialysis; with boiled milk, coagulation takes place in some cases only. The time of coagulation is inversely proportional to the amount of enzyme present. C. R. H.

Soluble Enzymes of the Bryony Root (*Bryonia dioica*). N. F. Girardet (*J. Pharm. Chim.*, 1924, [vii], **30**, 75—81).—Amylase, invertase, and peroxydase have been found in the root. It also contains a characteristic enzyme which acts on one or more of its constituents producing a dextrorotatory sugar. Basic ammoniacal lead acetate, but not neutral lead acetate, precipitates this enzyme.

D. R. N.

Utilisation of Dextrose in Mineral Media by Bacteria with reference to Acid Formation. J. S. Joffe and H. J. Conn (*Abstr. Bact.*, 1924, 8, 10—11).—In inorganic media with dextrose as a source of energy, various soil organisms utilise the constituents of the medium and impart a reaction irrespective of the course of dextrose fermentation. With ammonium dihydrogen phosphate (at p_H 6·6) the reaction became more acid; with sodium nitrate, alkaline. In the latter case, the nitrate was completely utilised, leaving sodium ions. Differential decomposition of the dextrose and adsorption phenomena also affect the final p_H.

A. A. E.

Enzyme in *Penicillium glaucum* which Hydrolyses Sucrose. H. von Euler, K. Josephson, and B. Söderling (*Z. physiol. Chem.*, 1924, **139**, 1—14).—The invertase contained in *Penicillium glaucum* (A., 1921, i, 482) cannot be removed from the cell by extraction with water, and no success has been attained in attempts to liberate it by autolysis. The optimum conditions of acidity for its action lie between p_H 4 and p_H 6, and thus differ from those of invertases of different origin. The "constant" calculated for a unimolecular reaction decreases rapidly during the reaction. The action of *P. glaucum* invertase, like that of taka-saccharase (Kuhn, A., 1923, i, 1033), is inhibited by dextrose, but not by lævulose. E. S.

Fermentation of Pentoses by *Bacillus granulobacter pectinovorum*. W. H. Peterson, E. B. Fred, and E. G. Schmidt (*J. Biol. Chem.*, 1924, **60**, 627—631).—Xylose and arabinose yield the same products as dextrose; slightly greater amounts of volatile acids and slightly smaller amounts of solvents (acetone, butyl alcohol) are, however, produced from the pentoses (cf. Speakman, this vol., i, 371). The fermentation of the pentoses is practically complete in 72 hours (cf. Robinson, A., 1922, i, 971). E. S.

Proteolytic Action of *Bacillus granulobacter pectinovorum* and its Effect on the Hydrogen-ion Concentration. W. H. Peterson, E. B. Fred, and B. P. Domogalla (*J. Amer. Chem. Soc.*, 1924, **46**, 2086—2090).—In the fermentation of maize mash a rapid hydrolysis of the proteins is produced by *Bacillus granulobacter pectinovorum*, from 50 to 75% of the total proteins being converted into soluble products during the fermentation, which is approximately complete in 3 to 4 days. There is little amino-acid or peptide formation during the first 24 hours, but after this the soluble protein and intermediate products increase more slowly and finally, after 48 hours, decrease, while amino-acid and peptide formation increase rapidly. At the end of 96 hours, the nitrogen is mainly in the form of proteoses, peptones, and peptides. Glutamic acid was isolated from the filtrate after phosphotungstic acid precipitation. Due to the buffer action of hydrolytic products and to acids with low dissociation, a high titratable acidity may be produced without much change in the hydrogen-ion concentration. R. B.

Decomposition of Cellulose by Various Groups of Micro-organisms of the Soil. H. Heukelekian (*Abstr. Bact.*, 1924, 8, 9).—Under similar conditions, fungi decompose cellulose in the form of filter-paper more readily than either bacteria or actinomycetes; a definite correlation appears to exist between the cellulose decomposed and the nitrogen assimilated, the ratio for most of the strong cellulose-decomposing fungi being 30 : 1. The results apply in the case of the decomposition of cellulose in the soil; when no available nitrogen is added, together with the cellulose, the amount of the latter decomposed will indicate to a certain extent the availability of the nitrogen of the soil. A. A. E.

Decomposition of Proteins and Amino-acids by Various Groups of Soil Micro-organisms. S. LOMANITZ (*Abstr. Bact.*, 1924, **8**, 9—10).—*Bacterium fluorescens* attacks amino compounds (glycine, alanine, and asparagine), but not casein in solution; *B. cereus* attacks casein, but not glycine or alanine, and asparagine only to a limited extent. *Actinomyces viridochromogenus*, *Trichoderma Köningi*, and *Zygorhynchus Mölleri* utilise all four compounds as sources of carbon and nitrogen. The amount of nitrogen assimilated by the organism depends on the presence or absence of dextrose. A. A. E.

Influence of Micro-organisms on the Carbon : Nitrogen Ratio of the Soil. S. A. WAKSMAN (*Abstr. Bact.*, 1924, **8**, 10).—The definite ratio (about 10 : 1) existing between the carbon and nitrogen contents of the soil is due to the activities of micro-organisms. Addition of organic matter results in its decomposition by soil micro-organisms, with the effect of narrowing down the original carbon : nitrogen ratio; whether nitrogen is made available or nitrogen starvation sets in depends on the carbon : nitrogen ratio of the organic matter of the soil, and the micro-organisms concerned. A. A. E.

Structure and Life-history of the Sulphur Bacteria. I. D. ELLIS (*Proc. Roy. Soc. Edinburgh*, 1923—1924, **44**, 153).

Preparation of Insulin. A. SORDELLI (*Compt. rend. Soc. Biol.*, 1924, **90**, 254; from *Chem. Zentr.*, 1924, i, 2446).—A method is described for the preparation of insulin in which the acid alcoholic extract of pancreas is precipitated with picric acid. G. W. R.

Insulin-like Substances from Beans and their Action on Carbohydrate Metabolism. M. EISLER and L. PORTHEIM (*Biochem. Z.*, 1924, **148**, 566—572).—Preparations made from extracts of dried beans (*Phaseolus multiflorus*) contain a substance which lowers the blood-sugar of rabbits without producing convulsions. Such extracts—including certain preparations devoid of insulin-like action—inhibit the action of salivary and taka-diastases on starch, and also lower the starch and sugar content, and increase the acetaldehyde content of pulped beans (*P. vulgaris*) when incubated with the latter at 36° in physiological saline. J. P.

Chemical Constitution of Insulin. A. CRUTO (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 42—45).—A highly purified preparation of "insulin sulphate" examined by the author was free from phosphorus and had the percentage composition: C, 47·73; H, 7·27; N, 14·53; S, 1·73; O, 22·84; H_2SO_4, 5·90. T. H. P.

Influence of Insulin on the Dextrose-fermenting Action of *Bacillus coli*. G. McGuire and K. G. Falk (*J. Biol. Chem.*, 1924, **60**, 489—490).—No influence was observed. E. S.

Fat-soluble Vitamins. XVII. Induction of Growth-promoting and Calcifying Properties in a Ration by Exposure to Ultra-violet Light. H. Steenbock and A. Black (*J. Biol. Chem.*, 1924, **61**, 405—422).—Food free from vitamin-*A* can be activated by exposure to the light of a mercury vapour lamp and is not subsequently inactivated by heating at 96°; muscle and liver from rats which have been exposed to ultra-violet light contain vitamin-*A*, whereas from non-irradiated animals these tissues do not contain this vitamin. C. R. H.

Concentration of Vitamin-*B*. P. A. Levene and B. J. C. van der Hoeven (*J. Biol. Chem.*, 1924, **61**, 429—443).—A series of attempts was made to concentrate vitamin-*B* by precipitation or adsorption with various reagents and subsequent recovery from the precipitate, using as starting material the fraction prepared according to Osborne and Wakeman (A., 1920, i, 208). Adsorption with kaolin was unsuccessful. A slight purification was effected by adsorption with Lloyd's reagent and subsequent extraction with alkali (p_H 9·0), also by precipitation with barium hydroxide and subsequent removal of barium with sulphuric acid. The best result was obtained by adsorption with silica gel; from the adsorbate the active material could be partly extracted at p_H 3·0, a larger and more active fraction being obtained by further extraction at p_H 9·0. C. R. H.

Spinacin, a New Protein from Spinach Leaves. A. C. Chibnall (*J. Biol. Chem.*, 1924, **61**, 303—308).—By the application of the author's method (A., 1923, i, 635) for the extraction of cytoplasmic material from leaf-cells, a new protein, "spinacin," has been isolated from the common spinach. The substance is free from carbohydrate, is insoluble in water and neutral salt solutions, but readily soluble in a small excess of either acid or alkali; it is precipitated by salts from either solution, more readily from the acid one; its isoelectric point lies between p_H 4·0 and 4·6. C. R. H.

Biochemical Hydrolysis of Rutin. Presence of Rutin in Plants and Identification of the Glucoside and its Hydrolysis Products. C. Charaux (*Bull. Soc. Chim. biol.*, 1924, **6**, 631—640, and 641—647).—A list of plants from which rutin may be extracted is given. The pure glucoside, $C_{27}H_{30}O_{16}$, crystallises from water in fine needles with $2H_2O$, and melts indefinitely at 188—190°. On heating on the water-bath with 4% sulphuric acid, an insoluble precipitate was obtained which was identified by means of its bromo derivative as quercetin. The acid mother-liquor, after removal of the quercetin, yields rhamnose and dextrose. Partial hydrolysis of rutin was brought about by an enzyme from the seeds of *Rhamnus utilis*; in this experiment the carbohydrate part of the molecule was obtained as a disaccharide ("rutinose") which was slightly dextrorotatory, softened at 140°, and melted at 189—192° (decomp.), giving dextrose and rhamnose on acid hydrolysis. C. R. H.

Glucoside Hydrolysable by Emulsin in the Genera, *Veronica, Euphrasia, Odontites, Bartsia,* and *Pentstemon.* M. BRAECKE (*Bull. Soc. Chim. biol.*, 1924, 6, 665—671).—Observations of the effect on the optical rotation and the reducing power of extracts of these plants brought about by emulsin show that they all contain glucosides hydrolysable by this enzyme. Invertase has, in most cases, no effect on the extracts. C. R. H.

Solanine Content of Potatoes. C. GRIEBEL (*Z. Unters. Nahr. Genussm.*, 1924, 47, 436—408).—In many parts of Germany the potatoes grown during the year 1922 contained an unusually large quantity of solanine (0·038 to 0·079%) and their consumption caused illness; when re-grown during 1923, these potatoes produced tubers of normal solanine content (0·005%). Experiments showed that the quantity of solanine in potatoes may be doubled by exposing the latter to light for 4 days, and it would appear that the poisonous potatoes had been unduly exposed during the harvest, transport, or storage. W. P. S.

Constituents of *Astragalus sinicus*, L. K. YOSHIMURA and S. FUJISE (*J. Chem. Soc. Japan*, 1924, 45, 32—41).—The fresh grass contained: water, 90·17%; protein, 2·19%; ether extract, 0·60% (fats, 0·25%, and colouring matters, 0·35%); fibre, 2·66%; soluble non-nitrogenous compounds, 3·41%, and ash, 0·97%. From an aqueous extract of 40 kg. of the grass, the following organic compounds were isolated: malonic acid, 2·7 g.; adenine hydrochloride, 1·5 g.; histidine, trace; arginine nitrate, 0·3 g.; choline chloroaurate, 1·5 g.; trigonelline hydrochloride, 0·12 g. No betaine was found. K. K.

Constituents of "Hang-ge." S. NAKAYAMA (*J. Pharm. Soc. Japan*, 1924, No. 509, 551—564).—The drug "Hang-ge" (Chinese: Pwan-hia) is the root nodule of *Pinellia tuberifera*, Ten., and is used as an anti-emetic. The powdered material was extracted first with ether, then with alcohol, and finally with water. The ethereal extract (1·02—1·10% of the fresh material) is composed of an ethereal oil and a fatty oil (semi-solid in ordinary temperature, iodine value 80·92, saponification value 133·32, acid value 1·91). On hydrolysis with alcoholic potash, the fatty oil gave about 20% of unsaponifiable substance, from which a phytosterol ($C_{26}H_{44}O,H_2O$, m. p. 136°, $[\alpha]_D^{20}$ −31·37°, acetate, m. p. 121°) was isolated. Among the saturated fatty acids, palmitic acid was detected. From the unsaturated acid fraction, an acid, $C_{18}H_{34}O_2$, m. p. 44°, b. p. 208—216°/3 mm., probably *iso*oleic acid, was isolated. From the alcoholic extract (1·25—3·90%), oxalic acid (0·29—0·38% of the material) was isolated and from the water extract (3·67—4·10%) a sugar. K. K.

New Constituent of *Atractylis ovata*, Thunb. S. Takagi and G. Hongo (*J. Pharm. Soc. Japan*, 1924, No. 509, 539—551).—By steam distillation of *Atractylis ovata*, Thunb. (*Compositæ*), a light yellow, viscous oil is obtained (d^9 0·985, $[\alpha]_D^9$ + 46·5°, acid value 0, saponification value 16·95). It slightly reddens fuchsin–sulphurous acid solution and reduces Fehling's solution when heated. When subjected to fractional distillation in a vacuum, crystals appear in the distillate (yield: 20% of the oil). The name *atractylon* is given to this substance (colourless plates, m. p. 42°, b. p. 131—132°/4 mm., $[\alpha]_D^{21}$ + 39·65°, d_4^{21} 1·0269 and n_D^{21} 1·52627). Its formula is $C_{14}H_{18}O$, and it can be recrystallised from methyl alcohol. The mother-liquor contains no atractylol, $C_{15}H_{26}O$ (cf. Gadamer and Amenomiya, A., 1903, i, 353). Atractylon is unstable in air, changing into a resin. With vanillin and hydrochloric acid, it gives a cherry-red coloration. The pine-shaving hydrochloric acid reaction gives a violet colour. It does not reduce Fehling's solution. It reacts violently with bromine in acetic acid solution, and contains no methoxyl. No acyl derivative could be obtained. It does not combine with hydroxylamine, phenylhydrazine, or semicarbazide, and could not be reduced with sodium and ethyl or amyl alcohol. From these results, atractylon is concluded to be an ether-like compound. Reduction with hydrogen in acetic acid solution, using platinum black as a catalyst, yielded *hexahydroatractylon*, $C_{14}H_{24}O$, a colourless, stable oil, b. p. 135—136°/4 mm., d_D^{20} 0·9919, $[\alpha]_D^{21}$ −34·36°, n_D^{20} 1·50186. K. K.

Constituents of the Tomato. I. K. Yoshimura and K. Nishida (*J. Chem. Soc. Japan*, 1924, 45, 57—65).—From an aqueous extract of 100 kg. of tomato (*Lycopersicum esculentum*, Mill., water content 96·01%), the following compounds were isolated: malic acid, 4·45 g.; citric acid, 4·70 g.; adenine hydrochloride, 1·20 g.; arginine, trace; trigonelline chloroaurate, 1·35 g.; choline chloroaurate 0·20 g. K. K.

Nitrogenous Compounds in Pumpkin and Cucumber. K. Yoshimura and K. Nishida (*J. Chem. Soc. Japan*, 1924, 45, 49—57).—The pumpkin contained 82% of water. Analysis of the dried substance gave the following results: protein, 13·23%; fats, 2·47%; crude fibre, 8·95%; soluble non-nitrogenous substance, 68·42%; ash, 6·93%. From the aqueous extract of 16 kg. of pumpkin, free from seeds, the following compounds were isolated: adenine hydrochloride, 0·25 g.; arginine nitrate, 1·68 g.; trigonelline hydrochloride, 0·50 g. On extracting 22 kg. of cucumber (water content 96·15%) with hot water, adenine hydrochloride, 0·27 g., and trigonelline chloroaurate, 0·5 g., were isolated. A trace of arginine was detected. K. K.

Microchemical Detection of Acetaldehyde in Fruits. C. Griebel.—(See ii, 791.)

Methylpentosans in Cereals. G. Testoni.—(See ii, 790.)

Nitrogenous Compounds in the Oil Cake of *Brassica campestris*, var. *Chinensis*, T. Ito. K. Yoshimura and S. Fujise (*J. Chem. Soc. Japan*, 1924, **45**, 42—49).—The cake contained 10·84% of water. Analysis of the dried material gave the following results: total nitrogen, 6·15%; protein nitrogen, 5·60%; non-protein nitrogen, 0·55%; fats, 13·47%; ash, 11·63%. From an aqueous extract of 40 kg. of the cake the following bases were isolated: adenine hydrochloride, 1·2 g.; arginine copper nitrate, 0·6 g.; choline hydrochloride, 43·3 g.; and betaine hydrochloride, 0·85 g. K. K.

Microchemical Detection of Mustard Oils. A. Pietschmann.—(See ii, 793.)

Nitrogenous Constituents of the Juice of the Alfalfa Plant [Lucerne]. I. Amide and Amino-acid Nitrogen. H. B. Vickery (*J. Biol. Chem.*, 1924, **60**, 647—655).—The filtrate obtained from the press-juice after raising the alcohol content to 53% (cf. Osborne, Wakeman, and Leavenworth, A., 1922, i, 99, 1104) has been fractionally precipitated with a variety of reagents and the distribution of nitrogen determined in each fraction. Amino-acids are present only in small amount and account for 13·6% of the total nitrogen in the filtrate; small quantities of polypeptides, as shown by the increase in amino-nitrogen after hydrolysis, are also present. Tyrosine and asparagine have been isolated in a pure state; the yield of the latter represented 35·7% of the amide-nitrogen and 5·82% of the total nitrogen in the filtrate. E. S.

Effects of the Method of Desiccation on the Nitrogenous Constituents of Plant-tissue. K. P. Link and E. R. Schulz (*J. Amer. Chem. Soc.*, 1924, **46**, 2044—2050).—Experiments with the leaves of the sugar-beet, the barberry, and maize, and with ears of maize show that the temperature of drying does not affect the total nitrogen content of the tissues but generally produces a decrease in the proportion of total soluble nitrogenous compounds, due to coagulation of the proteins. The effects of desiccation depend largely on the nature of the tissue involved. Drying at high temperatures (80° to 90°) causes a considerable decrease in water-soluble nitrogen, this effect being more pronounced with beet leaves and maize ears than with maize and barberry leaves. At lower temperatures (30° to 45°) proteolytic decomposition takes place, which in some cases is balanced by coagulation of the soluble nitrogenous constituents. At 65° a decrease in the amount of soluble nitrogen is the only significant alteration (cf. Tottingham, Schulz, and Lepkovsky, this vol., i, 598). R. B.

Effect of Titanium on Plant Growth. E. Blank and F. Alten (*J. Landw.*, 1924, **72**, 103—110).—The authors were unable to confirm the results of Němec and Káš (A., 1923, i, 1161) and find that the addition of sodium titanate may depress the dry weight of mustard and maize plants. This depression appears to be directly proportional to the amount of titanate added. O. O.

Have Green Plants the Power of Fixing Elementary Nitrogen from the Atmosphere? C. B. Lipman and J. K. Taylor (*J. Franklin Inst.*, 1924, **198**, 475—506).—Wheat and barley in culture solutions with and without nitrate nitrogen fix atmospheric nitrogen without bacterial intervention. Incomplete experiments suggest that *Bromus villosus* is able to fix nitrogen, but that peas cannot. Barley does not fix as much elementary nitrogen as wheat in the presence of nitrates in solution. In the case of wheat, there appears to be a minimum supply of nitrate nitrogen below which decrease in the amount of such nitrogen has no effect on the nitrogen content of the dry matter produced. O. O.

Significance of Oxygen for the Formation of Enzymes in Germinating Plant Seeds. A. Oparin and A. Bach (*Biochem. Z.*, 1924, **148**, 476—481).—The increases in the peroxydase, protease, and amylase contents of moistened wheat seedlings, kept for two days out of contact with oxygen, become more marked if oxygen be admitted. Autolysis of the material in the absence of oxygen causes a diminution in catalase, whilst in the presence of this gas a still greater diminution is noted. On subjecting the seedlings or extracts made from them to anodic oxidation the enzymes first increase to a maximum and then diminish in amount. Peroxydase is present in plant fibrin after tryptic digestion followed by anodic oxidation, but it is not detectable in the original material. A similar treatment of egg-albumin and crystallised plant-globulin yields negative results. J. P.

Can Measurements of Enzyme Action be Employed for Ascertaining the Vitality of Important Cultivated Plants? T. Bíčchy (*Fermentforsch.*, 1924, **8**, 135—166).—Comparison of the activity of the catalase contained in the expressed juice of the stems of potato plants grown under different conditions shows that this measurement may afford useful evidence regarding the vitality of the plant. It is suggested that this method of investigation be extended to other species. C. R. H.

Resistance to Disease in Plants. J. J. Willaman, C. A. Morrow, and A. K. Anderson (*Minnesota Agr. Expt. Sta., Ann. Rept.*, 1922, 35 pp.).—The principal products of metabolism of the flax wilt organism (*Fusarium lini*) are stated to be carbon dioxide and alcohol, with smaller amounts of organic acids.

Chemical Abstracts.

Apparently Specific Test for Tannins. A. H. Ware.—(See ii, 789.)

Influence of Electrolytes on the Total Surface of Soil Particles. L. Smolik (*Compt. rend.*, 1924, **179**, 211—213).—The effect of electrolytes on the hygroscopic behaviour of soils has been examined. The addition of an electrolyte apparently coagulates the soil colloids, and thus reduces the surface and the power of absorbing moisture. Removal of the electrolytes by washing has the converse effect. [Cf. *B.*, 1924, 920.] M. S. B.

Organic Chemistry.

Action of Ozone on Hydrocarbons with Special Reference to the Production of Formaldehyde. III. Action of Ozone on *n*-Hexane. E. W. Blair, T. S. Wheeler, and W. Ledbury (*J. Soc. Chem. Ind.*, 1924, **43**, 287—289T).—The action of ozone on boiling *n*-hexane yields formaldehyde, acetaldehyde, and other aldehydes up to *n*-hexaldehyde; acids up to *n*-hexoic acid (produced in greatest quantity); also traces of carbon monoxide and dioxide and water. *n*-Hexyl *n*-hexoate and other esters are also formed.

Action of Bromine on *n*-Hexane. E. W. Blair, W. Ledbury, and T. S. Wheeler (*J. Soc. Chem. Ind.*, 1924, **43**, 289—290T).—*p*-Dibromobenzene and *trans*-benzene hexabromide are produced when nitrogen carrying the vapour of either benzene or *n*-hexane is passed through bromine at the ordinary temperature. It is probable that the hexane is converted into *cyclo*hexane and then into benzene by oxidation.

Liberation of Hydrogen from Carbon Compounds. I. Interaction of Acetylene, Methyl Alcohol, and Formaldehyde with Fused Alkali Hydroxides. H. S. Fry, E. L. Schulze, and H. Weitkamp (*J. Amer. Chem. Soc.*, 1924, **46**, 2268—2275).—The reaction between dry acetylene and an equimolecular mixture of sodium and potassium hydroxides at 300—325° yields various quantities of orthocarbonates, but no acetates as reported by Feuchter (A., 1914, i, 406). The quantity of carbonate produced is approximately proportional to the amount of acetylene introduced into the alkali hydroxides, but owing to decomposition of the acetylene, evidenced by deposition of free carbon, the amounts of hydrogen and methane are not in accord with the equation $C_2H_2+4NaOH \longrightarrow H_2+CH_4+C(ONa)_4$. Minute traces of unsaturated hydrocarbons are also formed. Similarly, methyl alcohol yields a mixture of carbonates and hydrogen, the ratios of the amounts of methyl alcohol consumed and carbon dioxide and hydrogen produced being in agreement with the equation $MeOH+2NaOH \longrightarrow Na_2CO_3+3H_2$. Formaldehyde behaves similarly, the ratio of the amounts of aldehyde consumed and carbon dioxide and hydrogen produced according approximately with the equation $CH_2O+2NaOH \longrightarrow Na_2CO_3+2H_2$. The reactions are in accordance with the general type reaction, $R(H)_n+nMOH \longrightarrow R(OM)_n+nH_2$, and are analogous to the reactions between glycol and potassium hydroxide and resorcinol and sodium hydroxide. The mechanism of the reactions is suggested by the scheme $HC\vdots CH+2NaOH \rightarrow CHMe(ONa)_2$; $CHMe(ONa)_2+NaOH \rightarrow CMe(ONa)_3+H_2$; $CMe(ONa)_3+NaOH \rightarrow CH_4+C(ONa)_4$ (cf. Peters, this vol., ii, 174). The oxidation of cellulose by fused alkali hydroxides, yielding oxalates, conforms to the proposed type reaction. R. B.

Metallic Acetylides. II. Action of Acetylene on Metals. J. F. Durand (*Bull. Soc. chim.*, 1924, [iv], **35**, 1141—1144; cf. this vol., i, 602).—By the direct action of acetylene on the metal at 450—500° (cf. Novak, A., 1909, i, 865; 1910, ii, 778) the author has obtained *beryllium acetylide*, *cadmium acetylide*, and a new *aluminium acetylide*, probably BeC_2, CdC_2, and $Al_2(C_2)_3$, respectively, and the zinc acetylide, ZnC_2, previously described (A., 1923, i, 449). These acetylides, which have not been obtained free from carbon or excess of the metal, are distinguished from magnesium acetylide in not giving rise to allylene derivatives; on treatment with water or dilute hydrochloric acid, acetylene is the only hydrocarbon produced, except in the case of aluminium acetylide when some methane is probably also formed (cf. Kusnetzoff, A., 1907, i, 669). Gold, palladium, uranium, and mercury give no acetylide under these conditions, and no acetylene could be obtained from the deposited carbon. The action of acetylene on aluminium and lead amalgams etc., and of iron, lead, etc. on acetylene in acetone solution, gave inconclusive results. R. B.

Comparison of Molecular Volume Numbers. R. Lorenz and W. Herz.—(See ii, 823.)

Chlorination of Chloroform. H. Gault and R. Truffault (*Compt. rend.*, 1924, **179**, 467—469).—Chlorine is without action on chloroform in the dark or when exposed to red or yellow light, but light of shorter wave-length favours the reaction, the velocity of which is most marked in the ultra-violet region. Dry chlorides of calcium, zinc, or aluminium act in some degree as catalysts, but ferric chloride appears totally to inhibit the reaction. This is due to its absorption of the radiations of effective wave-length, as no chlorinating action occurs when a screen of ferric chloride solution is interposed. When in very dilute solution, absorption of the activating radiation is incomplete and a small yield of carbon tetrachloride is obtained. The velocity of the reaction increases with temperature. H. J. E.

Organic Reactions at the Surfaces of Dehydrogenating Catalysts. H. Adkins and W. A. Lazier (*J. Amer. Chem. Soc.*, 1924, **46**, 2291—2305; cf. this vol., ii, 159).—The behaviour of ethyl alcohol, ethyl acetate, acetal, ether, acetaldehyde, and acetic acid at the surfaces of various catalysts containing nickel, copper, iron, and zinc has been investigated with a view to determine whether the reactions taking place are dependent on the physical nature of the surface or are characteristic of the metal present. [illegible] types of nickel are produced through reduction by alcohol at 350—420° and by hydrogen at 300—400°. The former is at least twice as active as the latter in dehydrogenating alcohol and much more active in breaking down acetaldehyde to carbon monoxide and methane, practically no acetaldehyde being obtained from ethyl alcohol with this catalyst. In the hydrogenation of ethylene, it is only slightly superior, but with pure acetaldehyde, ethyl ether, and acetal it is many times as effective as nickel prepared with hydrogen. Neither catalyst is effective with ethyl acetate, whilst a catalyst reduced from nickel oxide by ethyl acetate itself is effective both against the ester and the alcohol; these facts, with the observations that nickel reduced with ethyl ether or acetal is reactive towards these compounds, whereas nickel reduced with hydrogen is not, lend some support to Boswell's theory of the activity of nickel catalysts. The evidence that oxygen must be present at a nickel surface in order that the nickel may function as a catalyst is inconclusive. If a nickel catalyst reduced by hydrogen is treated with oxygen, its activity towards dehydrogenation or decomposition is much increased, but this reactivation is not due to the addition of oxygen. Treatment of a hydrogen-reduced catalyst with oxygen followed by reduction with an organic reducing agent produces a much more effective catalyst than the original, the new catalyst producing a different proportion of reactions. A nickel catalyst reduced with alcohol does not lose its activity on treatment with hydrogen. The results obtained by passing a mixture of ethyl alcohol and acetic acid over nickel catalysts are in harmony with the activities when the two substances are reduced alone, the decomposition of ethyl alcohol being the more rapid reaction. The reactions under consideration are not successive reactions, the proportion of reaction products being determined by the nature of the catalyst, whilst the amount of reaction is dependent on variable factors such as time and temperature. The evidence indicates that the true catalyst is not a nickel oxide, but metallic nickel, and that the spacing of the active points is of fundamental importance, as it is in the case of non-reducible oxide catalysts. All nickel catalysts are characterised by their power of breaking carbon linkings, and this may be connected with the ability of nickel to pull electrons from their normal position between atoms.

When alcohol is passed over iron oxide obtained by drying precipitated ferric hydroxide or by igniting the nitrate or oxalate, the reactions involving the formation of methane and ethane and those of dehydrogenation occur in the proportion of 1 : 4 or 1 : 5. Iron oxide obtained from *methyl* or *ethyl ferrite*, however, behaved like reduced iron, yielding almost entirely a straight dehydrogenation to acetaldehyde and hydrogen. Copper catalysts obtained by ignition of copper nitrate, oxalate, and formate and by reduction of cuprous oxide give a similar straight dehydrogenation of ethyl alcohol. Zinc oxide obtained from zinc hydroxide dehydrogenates six times as much alcohol as it dehydrates, whilst with zinc oxide from *zinc* iso*propoxide*, the ratio dehydrogenation/dehydration is only 4/1, and in the latter case 5—6% of carbon dioxide is produced, whereas in the first case only 1—2% is formed. The catalyst from *zinc butoxide* is intermediate between these two catalysts. The oxide obtained from the *iso*propoxide gives results with acetaldehyde almost identical with those from iron oxide in the proportions of the reaction products, whereas the catalyst from zinc hydroxide gives 25% less carbon dioxide, 30% more carbon monoxide, and 40% less hydrogen. Generally, the catalyst from zinc *iso*propoxide is much the more active. The cases of zinc and ferric oxides are thus similar to alumina and titania in that the relative activities of the catalysts for different simultaneous reactions on their surfaces are determined by the solid compound which is converted into the catalyst, in contrast to nickel catalysts, the relative activity of which is determined by the process by which the nickel compound is reduced (cf. Kelber, this vol., ii, 244). The experimental results of Sabatier and Mailhe are criticised as inconclusive owing to their nickel having been partly reduced by hydrogen and partly by alcohol. R. B.

Catalytic Dehydration of Alcohol and Ether by Alumina. J. B. SENDERENS (*Bull. Soc. chim.*, 1924, [iv], **35**, 1144—1145).—The results obtained by Pease and Young (this vol., i, 363) have already been described by the author (A., 1909, i, 127; 1912, i, 406). R. B.

Odour and Chemical Constitution. A. MÜLLER (*Deuts. Parfümerie Ztg.*, 1923, **9**, 5—6; from *Chem. Zentr.*, 1924, i, 2778).—The *dimethyloctanols* prepared by reducing active citronellal and inactive citral with nickel and hydrogen have different odours, the alcohol from citronellal smelling like *iso*pulegol. Carefully purified inactive dimethylnonanol had a cruder and more intense odour than the active alcohol. F. A. M.

Density of Gaseous Dimethyl Ether. T. BATUECAS (*Compt. rend.*, 1924, **179**, 440—443).—The mean value of a series of twenty determinations of the weight of a litre of gaseous dimethyl ether under standard conditions is 2·1097 g. This is in agreement with the value obtained by Baume (A., 1908, ii, 372). The gas used was prepared by two different methods. H. J. E.

Velocity of Hydrolysis of Ethyl Ether. A. SKRABAL and H. AIROLDI.—(See ii, 842.)

Action of Chlorine on Trimethylene Trisulphide. J. GIRON (*Bull. Sci. Pharmacol.*, 1924, **31**, 25—27; from *Chem. Zentr.*, 1924, i, 2774).—On passing a stream of chlorine over methylene sulphide and fractionating the product, a substance, (?) $CH_2Cl·S·CHCl_2$, b. p. 85—86°/29 mm., d_4^{24} 1·6374, is obtained. F. A. M.

Ionisation of Some Organic Acids dissolved in Mixtures of Water and Ethyl Alcohol. M. DUBOUX and D. TSAMADOS.—(See ii, 827.)

Preparation of β-Chloropropionic Acid. C. MOUREU and R. CHAUX (*Bull. Soc. chim.*, 1924, [iv], **35**, 1360—1364; cf. A., 1917, i, 534; 1921, i, 495; 1922, i, 105).—Dry hydrogen chloride is passed into acraldehyde at −15° until the theoretical gain in weight has taken place. The product is then oxidised in small quantities at a time by adding it slowly, with agitation, to fuming nitric acid (*d* 1·49). At first, the temperature is kept between 30° and 35°, but the action is completed on the water-bath. The yield of β-chloropropionic acid averages 65%, but with specially pure nitric acid it may reach 70%. W. E. E.

Optically Active αβ-Dibromopropionic and αβ-Dichloropropionic Acids. P. KARRER and W. KLARER (*Helv. Chim. Acta*, 1924, **7**, 929—931).—By the action of cold nitrosyl bromide *d*-αβ-diaminopropionic acid is converted into d-αβ-*dibromopropionic acid*, b. p. 129°/9 mm., m. p. 64—66°, $[\alpha]_D^{20}$ +6·5° to +7·0° in water. In the same way, nitrosyl chloride gives d-αβ-*dichloropropionic acid*, b. p. 113°/12 mm., m. p. 36°, $[\alpha]_D^{20}$ +18·8°. In both cases, it is possible that racemisation has taken place. *d*-αβ-Dibromopropionic is transformed into *l*-glyceric acid. W. E. E.

Autoxidation of Crotonaldehyde. Preparation of Crotonic Acid. A. DUCHESNE and M. DELÉPINE (*Bull. Soc. chim.*, 1924, [iv], **35**, 1311—1317).—Oxygen is bubbled through three flasks of crotonaldehyde connected in series; the first two flasks are maintained at 70°. After the third or fourth day, the first flask is removed and its place taken by the second; the third flask takes the second place and a fresh flask of aldehyde is connected at the end. Besides crotonic acid (yield 45—50%), acetic acid and a resin are formed. In small quantities, ferric oxide and manganese hydroxide accelerate the oxidation, but foreign acids are still produced and the yield is little improved. Dilution of the crotonaldehyde with ether or benzene reduces the yield of acid obtainable; the presence of alcohol, water, or light petroleum (b. p. 100°) in sufficient quantity prevents oxidation altogether. W. E. E.

Fish Oils. Quantitative Analysis of Sardine Blubber. A. EIBNER and E. SEMMELBAUER (*Chem. Umschau*, 1924, **31**, 189—197; 201—209).—A sample of sardine blubber, forming a viscous, brownish-yellow oil which deposited crystalline fats at ordinary temperatures, had the following constants: iodine value, 136·0; acid value, 18·8; ester value, 179·8; saponification value, 194·9; unsaponifiable matter, 0·5%; ash, 0·18%. It contained clupanodonic acid, 12·7%; α-linoleic acid, 9·8%; *iso*linoleic acid, 10·1%; oleic acid, 28·6%; hydroxy-acids, 8·7%; saturated acids, 22·0%; glycerol, 4·1%; and cholesterol, 0·5%. Tsujimoto's formula for clupanodonic acid (A., 1923, i, 297) was confirmed, and the presence in the blubber of dipalmitostearin, oleodipalmitin, and probably the triglyceride of clupanodonic acid was established. [Cf. *B.*, 1924, 986.] F. G. W.

Velocity of Hydrolysis of Ethyl Orthoacetate. A. SKRABAL and M. BALTADSCHIEWA.—(See ii, 842.)

Mutual Relationship of the Formation of Oxalic and Citric Acids with Different Species of *Aspergillus niger*. C. WEHMER (*Ber.*, 1924, **57**, [*B*], 1659—1665).—The action of various species of *Aspergillus niger* on sugar solutions in the presence of potassium nitrate, potassium dihydrogen phosphate, magnesium sulphate, and calcium carbonate leads to the production of calcium oxalate and, frequently, of calcium citrate. The formation of calcium citrate is particularly noticeable when potassium nitrate is replaced by ammonium nitrate as source of nitrogen. The hypothesis that the production of oxalic acid from sucrose occurs through the intermediate formation of calcium hydrogen citrate is supported by the observation that oxalic acid is freely produced by the action of *A. niger* on solutions of sodium, ammonium, or calcium hydrogen citrates in which these salts are the sole source of carbon; normal calcium citrate does not undergo a similar change. With certain species of *Aspergillus*, notably *A. niger japonicus*, production of oxalic acid does not occur. Calcium hydrogen citrate is converted by this mould into the normal citrate, the citric acid appearing to be transformed directly into carbon dioxide; it is noticeable that the salt is never decomposed completely. Cessation of activity is attributed to the diminishing acidity of the solution; with moulds which yield oxalic acid, such diminution does not occur, since the utilised citric acid is replaced by oxalic acid. H. W.

Glutaconic Acids. XVII. Tendency towards Reversion to Type. C. K. INGOLD, J. H. OLIVER, and J. F. THORPE (*J. Chem. Soc.*, 1924, **125**, 2128—2136).—When mobile derivatives of the glutaconic acids are transformed into static derivatives, the latter exhibit a remarkable instability and tendency to revert to a mobile form. The reversion of static dibromo-additive products into glutaconic acids is believed to take the following course, $CO_2H{\cdot}CH_2{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CH_2{\cdot}CH{:}CBr{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H$, since intermediate compounds have been isolated. By exposure of ethyl aconitate to bromine vapour for 2—3 weeks, it is converted into ethyl αβ-dibromotricarballylate, which on distillation yields the *lactone* ester of *bromohydroxytricarballylic acid*, b. p. 205°/10 mm., and on hydrolysis with barium hydroxide, sodium carbonate, or methyl-alcoholic potassium hydroxide gives aconitic acid. When treated with cold alcoholic sodium ethoxide, the ethyl dibromo-ester yields ethyl α-bromoaconitate, which on hydrolysis gives rise to aconitic acid.

The tendency of the dibromides to regenerate the parent acids depends on the mobility of the acids produced. Glutaconic acid itself is the most mobile and can only be isolated in one form, and the labile form of the ester has a very transitory existence. Introduction of substituents in either the α- or β-positions decreases the mobility. Thus the normal form of α-methylglutaconic acid is converted into αβ-*dibromo-α*(or -γ)-*methylglutaric acid*, m. p.

178° (decomp.), by the action of bromine vapour; the acid yields normal α-methylglutaconic acid when hydrolysed. Similarly, normal β-methylglutaconic acid was transformed into *αβ-dibromo-β-methylglutaconic acid,* m. p. 142°, from which only the labile form of β-methylglutaconic acid is obtained by hydrolysis.

The tendency to reduction is suppressed by introducing two substituents, either in the αβ- or αγ-positions. αβ-Dimethylglutaconic acid, when exposed to bromine vapour, yields *α-bromo-αβ(or -βγ)-dimethylglutaric acid,* m. p. 115° (decomp.), whereas the corresponding αγ-dimethylglutaconic acid gives αβ-dibromo-αγ-dimethylglutaric acid, m. p. 134°; both bromo-acids are converted by the action of alkalis into hydroxylation products, and not into glutaconic acids.

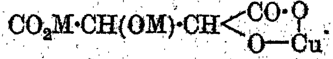
The reaction is confined to glutaconic acids and is not shown by static unsaturated acids of the αβ- and βγ-type. Thus, vinylacetic acid can be converted into crotonic acid and *cyclo*hexylideneacetic acid into *cyclo*hexeneacetic acid, but when their dibromides are treated with dilute alkalis the unsaturated acids are not regenerated.

In all these cases, the replacement of the halogen by hydrogen in presence of aqueous alkali hydroxide results in the formation of alkali hypobromite in solution. Reduction was carried out in alcoholic solution of sodium ethoxide. Under these conditions, ethyl bromoaconitate might yield ethyl ethylaconitate and sodium hypobromite or ethyl aconitate and ethyl hypobromite. That the latter course is the more probable has been shown by conducting an experiment in presence of ethyl malonate, which by oxidation consequent on reduction of the bromoaconitate gives ethyl ethanetetracarboxylate. C. J. S.

Metallic Hydroxy-acid Complexes. III. Constitution of Cuprimalates and Analogous Compounds. I. W. Wark (*J. Chem. Soc.*, 1924, **125**, 2004—2009).—The isomeric change from cupric malate to cuprimalic acid is regarded as merely due to the wandering of a hydrogen atom resulting in a structure in which the copper atom replaces one atom of hydrogen in an alcoholic hydroxyl group and one atom in a carboxyl group. This idea is extended to the structure of certain alkaline complexes containing copper. In disagreement with the view of Pickering, the constitution of potassium cupricitrate, $(C_6H_4O_7)_2K_6Cu,6H_2O$, is considered to be $(CO_2K{\cdot}CH_2)_2C(O\overset{b}{K}){\cdot}CO{\cdot}O{\cdot}Cu{\cdot}O{\cdot}C(CH_2{\cdot}CO_2K)_2{\cdot}CO_2K$, in which the potassium atom *b* imparts alkalinity to the compound. Similarly, to the alkaline cupriglycollate described by Pickering (T., 1911, **99**, 1347) is assigned the structure

$$OK{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}Cu{\cdot}O{\cdot}CH_2{\cdot}CO_2K,2H_2O.$$

The alkali derivatives of tartaric acid of the type $M_2CuC_4H_2O_6$, obtained by Bullnheimer and Seitz, have the structure



$$CO_2M{\cdot}CH(OM){\cdot}CH{<}\begin{array}{l}CO{\cdot}O\\ \quad\;\;\,|\\ O{-}Cu\end{array}.$$

A second type of complex, in which the copper atom replaces the hydrogen atom in two hydroxyl groups, is exemplified in the derivatives of monobasic monohydroxy-acids such as lactic and salicylic acids. C. J. S.

Rotatory Dispersion of Tartaric Acid. T. M. LOWRY and P. C. AUSTIN.—(See ii, 714.)

Condensation of Acetoacetic Esters with Malonic Esters. H. GAULT and H. KLEES (*Compt. rend.*, 1924, **179**, 600—601).—A preliminary note. Ethyl α-chloroacetoacetate and ethyl sodiomalonate do not interact until heated; then, after several hours on the steam-bath, ethyl acetate and ethyl ethane-ααβ-tricarboxylate are formed. Reaction takes place with ethyl α-bromoacetoacetate in the cold; the oily product contains a little (1—3%) ethyl ethane-ααβ-tricarboxylate, ethyl malonate (53%), and ethyl diacetylfumarate (?), m. p. 123°. Ethyl sodioacetoacetate and ethyl bromomalonate yield a little ethyl malonate and ethyl ethanetetracarboxylate, together with a *liquid*, b. p. 224—230°/10 mm., in the formation of which 2 mols. of ethyl acetoacetate and 1 mol. of ethyl malonate have taken part. W. A. S.

Biological Oxidation. III. The Oxide of the SH-Group and Oxidation by Means of Ethyl Peroxide. A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, **149**, 188—190).—Using a new preparation of thioglycollic acid the author has been unable to repeat his previous observations (this vol., i, 708) regarding the structure of the intermediate oxide formed by the acid, and the further possibility of the intermediate compound being a hydroperoxide is also dismissed. Ethyl peroxide in the presence of iron and oxygen at 37° oxidises α-hydroxy-acids, formic, acetic, and glycerophosphoric acids, whilst mono- and di-hydric alcohols, aldehydes, glycerol, acetone, mono- and di-carboxylic acids, and β-hydroxy-acids are not oxidised. J. P.

Functional Derivatives of α-Sulphobutyric Acid and the Rotatory Power of their Active Components. H. J. BACKER and J. H. DE BOER (*Rec. trav. chim.*, 1924, **43**, 420—433; cf. this vol., i, 708; also Backer, A., 1921, i, 855).—*Aniline butyranilide-α-sulphonate*, m. p. 253—256°, obtained by the action of excess of aniline on aniline sulphobutyrate, reacts with barium hydroxide or carbonate, yielding *barium butyranilide-α-sulphonate*. The latter, when treated with copper, cobalt, or nickel sulphate, yields the corresponding metallic *salt* of the butyranilide-sulphonic acid. p-*Toluidine butyro*-p-*toluidide-α-sulphonate*, m. p. 245—250°, p-*anisidine butyro*-p-*anisidide-α-sulphonate*, m. p. 242°, and p-*phenetidine butyro*-p-*phenetidide-α-sulphonate*, m. p. 261—262°, were prepared by heating the corresponding acid sulphobutyrate with excess of the base already present. On heating *o*-phenylenediamine sulphobutyrate, *benziminazole-2-propylsulphonic acid* is formed, of which the *barium* and *cobalt* salts are described. 3 : 4-Diaminotoluene sulphobutyrate similarly yields *methylbenziminazole-2-propylsulphonic acid*. Resolution of butyranilide-α-sulphonic and benziminazole-2-propylsulphonic acids into their optical isomerides [illegible] effected by means of their *strychnine* salts; in addition, the active *barium*, *copper*, *cobalt*, and *nickel* salts of the former acid and the *barium* and *cobalt* salts of the latter were obtained. Variation in molecular rotation with wave-length is shown diagrammatically for both aqueous and alcoholic solutions of copper and cobalt butyranilide-α-sulphonate; the curves exhibit some marked abnormalities. H. J. E.

Preparation of Acetone from Acetic Acid. I. M. MASHINO (*J. Chem. Ind. Japan*, 1924, **27**, 804—809).—Acetone is obtained when a mixture of acetic acid vapour and nitrogen is passed over heated granulated calcium oxide at 260—550°. The optimum temperature is 400—500°. The yield (about 54%) of acetone is best when acetic acid is passed at the rate of 7—10 g. per hour at 450°, but is only slightly decreased by passing the acid at the rate of 16 g. per hour at 550°. K. K.

Catalytic Reduction of Oximes in the Presence of Colloidal Palladium. W. GULEWITSCH [with B. SSEMENOWITSCH, S. KAPLANSKY, and L. BRONDE] (*Ber.*, 1924, **57**, [*B*], 1645—1653).—Ethyl β-aminobutyrate is not formed by the catalytic hydrogenation of ethyl β-oximinobutyrate in aqueous-alcoholic solution in the presence of colloidal palladium; the observed absorption of hydrogen is due to fission of the oxime and reduction of the liberated hydroxylamine to ammonia. Acetoxime and methyl ethyl ketoxime could not be reduced under similar conditions, although the potential activity of the catalyst remained unaltered. Benzaldoxime, on the other hand, yields a mixture of mono- and di-benzylamine, ammonia, and benzaldehyde (cf. Paal and Gerum, A., 1909, i, 381; Rosenmund and Pfankuch, this vol., i, 34); dibenzylamine is readily characterised by its *nitrate*, m. p. 194°. Benzophenoneoxime gives diphenylmethylamine, but acetophenoneoxime and dibenzylketoxime could not be reduced. Acetaldoxime and propaldoxime are reduced exclusively to the corresponding tertiary amines. Reduction takes place only at the commencement of the experiment; subsequently, when the reaction appears to proceed more slowly, the oxime probably becomes hydrolysed and the liberated hydroxylamine is converted into ammonia. The production of the tertiary amine is not due to elimination of ammonia from preformed, primary amine. H. W.

Diacetone [Di-*iso*propylidene] Compounds of Arabinose and Galactose. O. SVANBERG and S. W. BERGMAN (*Arkiv Kemi, Min., Geol.*, 1924, **9**, 1—16).—The monoacetone derivatives of arabinose and galactose are not formed by hydrolysis of the diacetone compounds. The action of sulphuric acid on an acetone solution of arabinose yields diacetonearabinose [arabinose di*iso*propylidene ether] (yield 92—93%), m. p. 41—42°, b. p. 85—87°/1 mm., 90—91°/2 mm., $[\alpha]^{18}_{\text{Hg yellow}}$ +5·5°±0·2 in water (cf. Fischer, A., 1895, i, 437), which is quantitatively hydrolysed by 0·5% hydrochloric acid (but not by 0·1—0·2% acid) to arabinose. It was found that α-galactose was not acted on by acetone and sulphuric acid, but β-galactose dissolved, and was converted into its di*iso*-

propylidene derivative, b. p. 126°/1 mm., $[\alpha]^{18}_{\mathrm{Hg\ yellow}}$ −46° in water (cf. Freudenberg and Hixon, A., 1923, i, 1179). On hydrolysis, it behaved like diacetonearabinose. Diacetonegalactose on oxidation with potassium permanganate gave a positive, but diacetoneglucose a negative phloroglucinol test; it may be concluded that in the former case the OH in position 6 is unsubstituted, so that oxidation to a glycuronic acid derivative occurs (cf. Karrer and Hurwitz, A., 1921, i, 767; Irvine and Patterson, T., 1922, **121**, 2146). F. M. H.

Examination of Photosynthetic Sugars by the Methylation Method. J. C. Irvine and G. V. Francis (*Ind. Eng. Chem.*, 1924, **16**, 1019—1020).—A sample of syrup prepared by photosynthesis from formaldehyde was found to contain no polysaccharides of the type, $C_6H_{10}O_5$, or ketoses, but to have an apparent methoxyl content of 9—12%. Part of the reducing power to Fehling's solution was due to substances other than sugars. The syrup was purified by drying at 80° under a pressure of 0·2 mm. of mercury and was then subjected to methylation, whereby a fraction was obtained with a methoxyl content of 54·5% and a molecular weight of 232. After hydrolysis, the composition of the product closely corresponded with tetramethylhexose. It is deduced that the original proportion of hexoside present could not exceed 10%. The bulk of the syrup (to the extent of at least 80%) consists of non-sugar compounds which contain hydroxyl groups. C. I.

The Glucose of Sucrose. H. Colin and A. Chaudun (*Bull. Soc. Chim. biol.*, 1924, **6**, 625—630).—Polarimetric measurements show that the dextrose produced in the inversion of sucrose has at first a higher rotatory power than ordinary dextrose, but rapidly attains the normal value; it is therefore probably first split off from the sucrose molecule as α-glucose. C. R. H.

Preparation of β-Methylglucoside. H. H. Schlubach and K. Maurer (*Ber.*, 1924, **57**, [*B*], 1686—1687).—β-Methylglucoside is the primary product of the methylation of dextrose by Haworth's method (T., 1915, **107**, 8), but its isolation from the product of the reaction is rendered difficult by the presence of sodium methyl sulphate. Separation may be readily effected if the dry product is acetylated with acetic anhydride and pyridine and the mixture poured into ice-water. Sodium methyl sulphate passes into solution, whereas tetra-acetyl-β-methylglucoside is precipitated in the homogeneous condition and is subsequently hydrolysed to β-methylglucoside, the yield being about 40%. H. W.

Inversion of Sucrose and Determination of Hydrion Concentration. M. Duboux.—(See ii, 842.)

Apparent Concentration of the Hydrogen Ion in Solutions Containing Sucrose. T. W. J. Taylor and R. F. Bomford ([illegible] *Chem. Soc.*, 1924, **125**, 2016—2017).—By means of the hydrogen [illegible] method, the apparent concentration of the hydrogen [illegible] of sucrose undergoing inversion with hydrochloric acid in presence of sodium chloride has been determined. The *E.M.F.* slowly falls to a constant value about 1% smaller than the initial value of the cadmium cells employed, and hence the apparent hydrogen-ion concentration increases by about 7% during the inversion. C. J. S.

Mutarotation Lag in Sucrose Inversion. S. W. PENNYCUICK (*J. Chem. Soc.*, 1924, **125**, 2049—2063).—It is deduced mathematically that the lag in mutarotation when sucrose is inverted in presence of acids is not inappreciable. The method adopted for following the inversion before mutarotational equilibrium is established consists in chilling a portion of the solution to 0°, when inversion is practically stopped, and determining the rotation at this temperature. To determine the rotation after equilibrium, inversion is arrested in a portion of the reaction mixture by addition of sodium hydroxide, after which it is cooled to 0° and a reading taken. It is shown that after a brief interval of time the lag becomes strictly proportional to the concentration of the remaining sucrose, and that the graphs of log $(\lambda_t-\lambda_\infty)$, with and without lag, respectively, against t, become strictly parallel, both having the slope k_1, the inversion constant.

The usual method of following the inversion while the lag is present gives the correct value of k_1 if certain precautions are observed, but the curve log $(\lambda_t-\lambda_\infty)$ with lag against time does not extrapolate to log $(\lambda_0-\lambda_\infty)$ at $t=0$, but to log $\{\lambda_0-\lambda_\infty+A(R+S)\}$, where $R+S$ is the total lag constant under the given conditions, k_1 being given by $1/t \log [\lambda_0-\lambda_\infty+A(R+S)]/(\lambda_t-\lambda_\infty)$. The short-interval formula also gives the correct value of k_1 (whether the lag is appreciable or not), provided it is not applied at the initial stages of the inversion. C. J. S.

Action of Ultra-violet Radiations on Solutions of Sucrose. P. BEYERSDORFER and W. HESS (*Ber.*, 1924, **57**, [*B*], 1708—1711).—The photochemical decomposition of $M/8$, $M/2$, and $2M$ solutions of sucrose in water has been investigated at 20°, 70°, and 100°, the course of the change being followed by observations of the optical rotation, acidity, and reducing power of the solutions. Reaction is scarcely appreciable at 20°, but the rate increases first slowly and then rapidly with increasing temperature. The photochemical degradation of sucrose is almost completely inhibited by the presence of chlorophyll or, to a less extent, of green-PLX. Manganese chloride, potassium chloride, potassium bromide, and potassium iodide have little influence on the change, which, however, scarcely occurs in the presence of sodium acetate; this result is not surprising, since the latter salt is known to prevent inversion of sucrose. The sucrose molecule is so stable towards the action of light of short wave-length that the union of its component parts by an oxygen atom appears improbable. On the other hand, lævulose is considerably more rapidly decomposed than dextrose. The products of the decomposition of sucrose are carbon monoxide, carbon dioxide, hydrogen, methane, organic acids, aldehydes, ketones, and alcohols, together with condensation products of the type of dextrin and caramel. A crystal of sucrose when exposed to ultra-violet rays at 70° becomes coated on the exposed surface with a brown layer of caramel. The prolonged exposure of sucrose solutions to ultra-violet rays appears to yield sensibly the same products as are obtained by the dry distillation of sugar. H. W.

Variation of the Optical Activity of Sucrose on Heating. M. A. Rakusin and A. N. Nesmejanov (*Z. Unter. Nahr. Genussm.*, 1924, **48**, 151—152).—Commercial sucrose, m. p. 178—183°, $[\alpha]_D$ +65·33°, was caramelised by heating first to a temperature above the melting point and then maintaining at a lower temperature for varying lengths of time. Experiments were carried out at 160° to 190° for periods up to 4 hours. In all cases decrease of the rotatory power was observed varying with the temperature and duration of the experiment. After heating at 180° for 30 mins., the sugar was rendered optically inactive; after 2 hours at 150° the rotatory power was $[\alpha]_D$ +13·2°, and after 4 hours at 140°, $[\alpha]_D$ +21·0°. G. S. W.

Trihexosan. A. Pictet and R. Salzmann (*Helv. Chim. Acta*, 1924, **7**, 934—935).—The trihexosan obtained as the ultimate product of depolymerisation of starch by heat is hydrolysed by emulsin to dextrose and a dihexosan, m. p. 209—210° (decomp.), $[\alpha]_D$ +133·2°, which may be identical with the product of Pringsheim and Wolfsohn (this vol., i, 714). At present, it seems that the trihexosan is a β-glucosyldihexosan. W. E. E.

A Hexahexosan Obtained from Starch. A. Pictet and P. Stricker (*Helv. Chim. Acta*, 1924, **7**, 932—933).—Potato starch is heated at 200° with glycerol (Pictet and Jahn, A., 1922, i, 987) until the red coloration given with iodine is at its brightest, whereby a *hexahexosan*, decomp. about 225°, is isolated as a white, amorphous powder; it does not reduce Fehling's solution. When heated with acetic anhydride and sodium acetate it gives the trihexosan nona-acetate described by Pictet and Jahn (*loc. cit.*). W. E. E.

Hydrolysis of Starch by Salts. III. Hydrolysis by Inorganic Catalysts (Artificial Oxydases). W. Biedermann and C. Jernakov (*Biochem. Z.*, 1924, **149**, 309—328).—The hydrolysis of starch and the amyloses by salts of the heavy metals such as iron, copper, and manganese in the presence of hydrogen peroxide, and the typical "salt hydrolysis" shown by the chlorides and bromides of the alkali and alkaline-earth metals, suggest a parallelism between such hydrolytic actions and the oxydase- or peroxydase-like action of the salts towards guaiacum and other oxydase reagents. Manganese chloride may act on guaiacum and on starch in the absence of hydrogen peroxide and its action is therefore analogous to that of the alkali metals. J. P.

Polysaccharides. XXVIII. Reserve Cellulose (Lichenin). [illegible] and M. Staub (*Helv. Chim. Acta*, 1924, **7**, 928—929).—[illegible] of the preparations examined contained only 0·0055%

of phosphorus, it is certain that lichenin contains that element; the small proportion may be due to the action of large amounts of boiling water used to purify the lichenin. The ash of lichenin amounted to 0·9—1%, and contained much calcium, a little magnesium and iron, and only traces of silicic acid. When lichenin is quickly distilled at 12 mm., *l*-glucosan is obtained. W. E. E.

Proposed Definition of "Cellulose." P. Klason (*Papier-Fabr.*, 1924, 22, 373—377).—Two reagents are proposed for the complete removal of lignin from wood under conditions such that the cellulose residue remains constant in weight even after excessively prolonged digestion. They are both made up with 80 g. of sodium hydrogen sulphite per litre, but the weaker one contains 200 c.c. and the stronger 500 c.c. of *N*-hydrochloric acid per litre. The wood is digested continuously at 98°, the liquor being siphoned off and renewed every 4 days, until the residue is substantially constant in weight and free from lignin. With the weaker acid, spruce wood in chips or rasped yields 54% of cellulose after 9—12 days' digestion, but with the stronger acid, the yield from rasped wood is about 7% lower, whereas that from chipped wood is only 1·5% lower. Hence it is suggested that spruce wood contains two types of cellulose, one resistant to the stronger acid and corresponding with crystalline cellulose and the other resistant only to the weaker acid and corresponding with amorphous cellulose. In the natural condition, the crystalline cellulose protects the amorphous, but when the cells are ruptured by rasping this protection ceases. The degree of protection of the less resistant cellulose by the more resistant varies according to the species, and this protection is less complete in beech wood than in spruce wood. Cotton cellulose also resists the weaker acid, but breaks down, yielding only 90·5% residue with the stronger acid. The use of the weaker acid under the above conditions is suggested as the basis of an analytical definition of "cellulose." [Cf. *B.*, 1924, 976.] J. F. B.

Preparation of Cellulose Acetates. A. Caille (*Chim. et Ind.*, 1924, 12, 441—448).—A suitable mixture for the acetylation of 100 g. of cotton consists of 600 g. of 44·8% acetic anhydride with 15 g. of sulphuric acid. Avoiding rapid rises of temperature, the cotton goes smoothly into solution in about 6 hours with a maximum temperature of 38°. Higher temperatures yield products of low viscosity; smaller quantities of sulphuric acid involve prolonged periods of acetylation and inferior esterification. During the primary acetylation, the proportions of combined acetic and sulphuric acids increase steadily until the product, precipitated at the stage when the cotton fibre is entirely dissolved, contains 66—67% of acetic acid and 0·97% of sulphuric acid. These products are mixed acetic–sulphuric acid esters, and the secondary modification, induced by the introduction of 20 g. of water to the acetylated mixture, consists of an acid hydrolysis of the sulphuric acid ester. The stability of the ultimate cellulose acetate depends on the elimination, as completely as possible, of the combined sulphuric acid groups. This may be promoted by a secondary hydrolysis of the precipitated solid by digestion with 0·25% sulphuric acid at 75°. The acid function of the sulphuric acid ester is capable of neutralisation by mineral bases yielding ester salts, so that products washed with calcareous water are far more stable than those washed with distilled water. J. F. B.

Constitution of the Anhydrides of Glutamic Acid. A. Blanchetière (*Bull. Soc. chim.*, 1924, [iv], **35**, 1317—1325).—The results of biuret tests on the tri*cyclo*peptide from glutamic acid (A., 1923, i, 12) are sometimes positive and sometimes negative. This is explained if the tri*cyclo*peptide gives rise to the two forms of glutamylglutamic acid,

I. $CO_2H\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H$,

II. $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H$,

which are theoretically possible. Actually, when the tri*cyclo*peptide is hydrolysed with sodium or barium hydroxide, a crystalline glutamylglutamic acid is obtained together with a gum which is thought to be the second form of the acid. According to the results of the biuret reaction, the crystalline form has the structure I. W. E. E.

Formaldehyde Compounds of Simple Amino-acids. H. Krause (*Z. physiol. Chem.*, 1924, **139**, 216—218).—Polemical (cf. Krause, A., 1919, i, 67; Bergmann, Jacobsohn, and Schotte, this vol., i, 19). C. R. H.

Carbamide and Guanidine Derivatives of Aliphatic Sulphonic Acids. II. R. Andreasch (*Monatsh.*, 1924, **45**, 1—7).—The action of potassium sulphite on certain bromoacylcarbamides and on chloroacetamide is described.

In completion of earlier work (A., 1923, i, 546), the *barium* salt ($+2H_2O$) of sulphoacetylcarbamide is described. α-Bromopropionylcarbamide was converted by aqueous-alcoholic potassium sulphite into the *potassium* salt ($+1\frac{1}{2}H_2O$) of α-sulphopropionylcarbamide. Interaction of ethyl bromopropionate and thiocarbamide in alcoholic solution formed the *hydrobromide* of methylthiohydantoin. The corresponding hydrochloric acid solution was oxidised with potassium chlorate at 50—60° to the potassium salt of α-sulphopropionylcarbamide. Aqueous methylthiohydantoin hydrobromide treated with bromine at 60° followed by barium carbonate gives barium α-sulphopropionate, doubtless formed by hydrolysis of the expected sulphonate of propionylcarbamide. By heating phenylcarbamide with bromopropionyl bromide at 135—155°, *α-bromopropionylphenylcarbamide*, m. p. 162°, was obtained. Its interaction with potassium sulphite gave the *potassium* salt ($+H_2O$) of α-sulphopropionylphenylcarbamide. By heating α-bromo*iso*valeryl chloride and ethylcarbamide, there was obtained *α-bromo*iso*valerylethylcarbamide*, m. p. 110° (cf. D.R.-P. 185962). Potassium sulphite [illegible] the bromine by hydrogen, giving *ethyl*iso*valerylcarbamide*, [illegible]. Similarly, α-bromo-α-ethylbutyrylcarbamide gave [illegible]carbamide, m. p. 205°.

With potassium sulphite, the halogen in halogen derivatives of acid amides is readily replaced by HSO_3. Thus chloroacetamide yields the *potassium* salt of sulphoacetamide. *Sodium* and *ammonium* salts are prepared analogously. F. M. H.

Derivatives of Methylstannonic Acid. II. H. LAMBOURNE (*J. Chem. Soc.*, 1924, **125**, 2013—2015).—Penta-acyl derivatives of the type

$$SnMe(O{\cdot}COR)_2{\cdot}O{\cdot}SnMe(O{\cdot}COR){\cdot}O{\cdot}SnMe(O{\cdot}COR)_2,$$

have been obtained by the action of dichloroacetic, propionic, *n*-butyric, and *iso*butyric acids on methylstannonic acid, R being $CHCl_2$, Et, Pr^{α}, or Pr^{β}, respectively. The *pentadichloroacetyl* compound has m. p. 235—240° (decomp.). The *pentapropionyl* compound melts at 156—157°, solidifies again at 160°, and remelts at about 240°. The *pentabutyryl* compound and *pentaisobutyryl* compound have m. p. 105° and 194°, respectively.

The propionyl, butyryl, and *iso*butyryl penta-acyl derivatives when hydrolysed with alcohol yield hexa-acyl derivatives, regarded as having a cyclic structure.

The *hexapropionyl* compound partly melts at about 246° (decomp.), and is completely hydrolysed to methylstannonic acid on repeated boiling with alcohol. The *hexabutyryl* and *hexaisobutyryl* compounds have m. p. 180° and about 260°, respectively.

C. J. S.

Magnesium Acetylenyl Bromide. J. SALKIND and A. ROSENFELD (*Ber.*, 1924, 57, [*B*], 1690—1692).—Magnesium acetylenyl bromide, $CH{:}C{\cdot}MgBr$, is almost the sole product of the action of acetylene on magnesium and bromobenzene in the presence of ether if the boiling solution is continuously saturated with the gas during the whole course of the reaction. It is converted by acetophenone into *γ-phenyl-Δ^{α}-butinen-γ-ol*,

$$CMePh(OH){\cdot}C{:}CH,$$

an almost colourless liquid which cannot be distilled (the *copper* derivative is described) together with smaller amounts of the βε-diphenyl-Δ^{γ}-hexinene-βε-diols. H. W.

Stereoisomeric Forms of Decahydronaphthalene (Decalene). F. EISENLOHR and R. POLENSKE (*Ber.*, 1924, 57, [*B*], 1639—1644).—*cis*-Decahydronaphthalene, b. p. 193°/768 mm., $d_4^{20\,\text{vac.}}$ 0·8953, n_{α}^{20} 1·47817, is prepared by the action of a solution of sodium in absolute alcohol at 200° on *cis*-β-decahydronaphthalenesemicarbazone, m. p. 183°. Particularly if the alcohol used contains a trace of water, the hydrocarbon is accompanied by a considerable proportion of *cis*-decahydro-β-naphthol, which is transformed by potassium hydrogen sulphate at 200° into *cis*-octahydronaphthalene, b. p. 194°/771 mm., $d_4^{20\,\text{vac.}}$ 0·9090, n_{α}^{20} 1·49124. The unsaturated hydrocarbon is smoothly hydrogenated in ethereal solution in the presence of spongy platinum to *cis*-decahydronaphthalene, the physical constants of which agree with those of the product described above. *trans*-β-Decahydronaphthalonesemicarbazone (cf. Häckel, this vol., i, 32) is converted similarly by sodium ethoxide solution at 210° into a mixture of *trans*-decahydro-β-naphthol and *trans*-decahydronaphthalene, b. p. 185°/756 mm., $d_4^{20 \text{ vac.}}$ 0·8823, n_α^{20} 1·47218. The hydrocarbon having almost identical physical constants is also prepared by the hydrogenation of *trans*-octahydronaphthalene, b. p. 189°/768 mm., $d_4^{20 \text{ vac.}}$ 0·9009, n_α^{20} 1·48504, which is derived from *trans*-decahydro-β-naphthol, m. p. 75° (cf. Häckel, *loc. cit.*), by the action of potassium hydrogen sulphate. The optical constants of the authors' *cis*-decahydronaphthalene agree closely with those of the specimens prepared by Häckel (*loc. cit.*) and Willstätter and Seitz (this vol., i, 628). This is not the case with the *trans*-derivatives. It appears, therefore, that the product of the hydrogenation of naphthalene in the presence of nickel contains some component other than *trans*-decahydronaphthalene which tends to accumulate in the fractions of lowest boiling point. H. W.

Internal Structure of Crystallised Carbon and Benzene. J. Beckenkamp.—(See ii, 754.)

Mechanism of Substitution Reactions in the Aromatic Nucleus. E. de B. Barnett and J. W. Cook (*Rec. trav. chim.*, 1924, **43**, 262—265).—The possibility is considered of the formation of *cis* and *trans* geometrically isomeric unstable additive compounds in substitution reactions in the aromatic nucleus. The facts that *p*-chlorobromobenzene is almost the sole product in the bromination of chlorobenzene, no *p*-dibromobenzene being formed, and that bromonitrobenzene is alone produced in the nitration of bromobenzene, are explained by assuming that the intermediate additive compound has the *trans* configuration in each case. The type of isomerism here assumed is analogous to the isomerism of the esters of $\Delta^{2:5}$-dihydroterephthalic acids established by Baeyer. In the anthracene series, but not in the benzene series, several such additive compounds, for instance, the esters of nitrodihydroanthranol, have been isolated. J. K.

Replaceability of the Halogen Atom in Chloro- and Bromo-4-nitro-2-cyanobenzene. H. P. Baudet (*Rec. trav. chim.*, 1924, **43**, 707—726).—The reactivity of the halogen atom in these compounds is studied and compared with that of the halogen in chloro- and bromo-2 : 4-dinitrobenzenes and in chloro- and bromo-2-nitro-4-cyanobenzenes. In this way, the influence of the cyano group on the reactivity of the adjacent halogen atom is estimated. The reactivity of the chlorine in chloro-4-nitro-2-cyanobenzene is demonstrated by its direct replacement to give the following compounds: 4-nitro-2-cyanoanisole; 4-nitro-2-cyanophenetole; 4-*nitro*-2-*cyanodiphenyl ether*, m. p. 129° (by the action of phenol and sodium ethoxide); p-*nitro*-2-*cyanoaniline*, m. p. 209°; 4-*nitro*-2-*cyanomethylaniline*, m. p. 187°, which gives with concentrated nitric acid 4 : 6-*dinitro*-2-*cyanophenylmethylnitroamine*, m. p. 100°; 4-*nitro*-2-*cyanoethylaniline*, m. p. 144°, which gives 4 : 6-*dinitro*-2-*cyanophenylethylnitroamine*, m. p. 89°; 4-*nitro*-2-*cyanodimethyl*-

aniline, m. p. 110°; 4-nitro-2-cyanodiphenylamine, m. p. 172° (by the action of aniline); *4-nitro-2-cyanophenyl-*m*-tolylamine*, m. p. 142°; *4-nitro-2-cyanophenyl-*p*-tolylamine*, m. p. 218°; *4-nitro-4'-amino-2-cyanodiphenylamine*, m. p. 204° (by the action of phenylhydrazine); 4-nitro-2-cyanophenylhydrazine (by the action of hydrazine hydrate), giving *benzaldehyde-4-nitro-2-cyanophenylhydrazone*, m. p. 206°; *4-nitro-2-cyanohydrazobenzene*, m. p. 236°. Aniline, phenylhydrazine, and the toluidines react more readily with chloro-4-nitro-2-cyanobenzene than with chloro-2-nitro-4-cyanobenzene. With chloro-4-nitro-2-cyanobenzene, *p*-toluidine reacts more readily than *o*-toluidine, but less readily than *m*-toluidine. Methylaniline has no action on chloro-4-nitro-2-cyanobenzene. 4-Nitro-2-cyanophenylhydrazine has no action on acetone, whereas *p*-nitrophenylhydrazine readily reacts. Measurements of the velocity constants of the reaction between sodium methoxide or ethoxide and chloro- or bromo-4-nitro-2-cyanobenzene in absolute alcohol are given. Chlorine is more readily replaced than bromine and the velocity constant for sodium methoxide is smaller than that for sodium ethoxide. When the 2-nitro group of chloro-2 : 4-dinitrobenzene is replaced by a cyano group, the velocities of the actions of both sodium methoxide and ethoxide are decreased. Interchange of the cyano and nitro groups of the halogeno-4-nitro-2-cyanobenzenes reduces the velocity constants to about one-nineteenth. The velocity of the reaction of *p*-chloronitrobenzene with sodium methoxide is about 1/7500 of the velocity of the reaction of chloro-4-nitro-2-cyanobenzene with the same substance. In 90% alcohol, the velocity of the action of sodium methoxide on the halogeno-4-nitro-2-cyanobenzenes is greater than in absolute alcohol; the increase is greater for the chloro compound than for the bromo compound. On the other hand, with sodium ethoxide in 90% alcohol, *k* is smaller and the decrease is greater for the chloro compound than for the bromo compound. Measurements of *k* are given for the action of sodium methoxide on chloro-2 : 4-dinitrobenzene in mixtures of methyl alcohol and water. As the proportion of water in the medium is increased, a maximum in the value of *k* is reached; this occurs the sooner the higher the temperature. W. E. E.

Monochlorotrinitrobenzenes and the Replacement of their Substituents. P. G. Van de Vliet (*Rec. trav. chim.*, 1924, **43**, 606—635).—*Chloro-3 : 4 : 5-trinitrobenzene*, m. p. 168°, is obtained by the action of a mixture of nitric oxide and nitrogen peroxide at 0° on 4-chloro-2 : 6-dinitroaniline (from 1 : 4-dichloro-3 : 5-dinitrobenzene and alcoholic ammonia) mixed with concentrated nitric acid.

Chloro-2 : 3 : 5-trinitrobenzene is obtained from aceto-*m*-nitroanilide by nitrating with fuming nitric acid (*d* 1·52) in the presence of sulphuric acid and hydrolysing the 2 : 3-dinitroacetanilide separated from the resulting mixture of three isomerides; the dinitroaniline is diazotised, converted by cuprous chloride into chloro-2 : 3-dinitrobenzene, and nitrated in the presence of fuming sulphuric acid. The semi-solid product is separated into an oil and *chloro*-2 : 3 : 5-*trinitrobenzene*, m. p. 105—106°. Its structure is confirmed by conversion into chloro-3 : 5-dinitroaniline.

Chloro-2 : 3 : 4-*trinitrobenzene*, m. p. 68°, is prepared from the oil resulting from the above nitration, and its structure is confirmed by its conversion into a chlorodinitroaniline which yields chloro-2 : 4-dinitrobenzene.

Chloro-2 : 3 : 6-trinitrobenzene is not formed in the nitration of chloro-2 : 3-dinitrobenzene, and seven other methods of preparing this isomeride were tried unsuccessfully.

Den Hollander (A., 1920, i, 538) claims to have prepared 1 : 2-dichloro-3 : 6-dinitrobenzene (m. p. 60°). His experiments were repeated, starting from a mixture of 2 : 3- and 2 : 5-dinitroacetanilide. After hydrolysis, the 2 : 5-dinitroaniline (m. p. 138°) was dissolved in concentrated hydrochloric acid and treated with potassium chlorate. The mixture of chlorodinitroanilines thus obtained was diazotised and the diazo compounds were treated with cuprous chloride solution. 1 : 4-Dichloro-2 : 5-dinitrobenzene was isolated, and 1 : 4 : 6-trichloro-2 : 5-dinitrobenzene (m. p. 60°) was obtained from the mother liquor (A., 1921, i, 549).

To study the behaviour of the chlorotrinitrobenzenes towards sodium methoxide, the reaction mixture is poured into water and this is tested for chlorine and nitrite ions. In this way, it is shown that, in the following compounds, only the groups mentioned are replaced by methoxyl: chloro-2 : 4 : 6-trinitrobenzene, chloro; chloro-3 : 4 : 5-trinitrobenzene, 4-nitro; chloro-3 : 4 : 6-trinitrobenzene, chloro and 3-nitro; chloro-2 : 3 : 5-trinitrobenzene, 2-nitro; chloro-2 : 3 : 4-trinitrobenzene, chloro and 3-nitro. In the action of sodium methoxide on 1 : 3-dichloro-2 : 4-dinitrobenzene, it is the 3- and not the 1-chlorine atom which is replaced.

Owing to the considerable velocities developed in the reactions between sodium methoxide and the chlorotrinitrobenzenes all quantitative experiments were carried out at 0°. In the cases of the 1 : 2 : 4 : 6-, 1 : 3 : 4 : 6-, and 1 : 2 : 3 : 5-isomerides, the velocities were too great to be determined. For the 1 : 3 : 4 : 5-isomeride, $k=7{\cdot}5$ (approx.), and for the 1 : 2 : 3 : 4-isomeride, $k=10{\cdot}7$ (approx.), the constant being calculated from the formula $dx/dt=k(a-x)^2$.

Den Hollander's rules (*loc. cit.*) for the action of sodium methoxide on chloronitro derivatives of benzene prove to be of very limited application, and the following empirical conclusion is drawn. When sodium methoxide reacts with chloronitrobenzene derivatives, the substituents which are *meta* with respect to a nitro group tend to be inactive, whilst those that are *ortho* or *para* with respect to a nitro group tend to be replaced. It is concluded that the introduction of a nitro group into a chloronitro derivative of benzene causes a much greater increase in the reactivity of the substituents than does the introduction of a chlorine atom. W. E. E.

Mononitration of p-Chlorotoluene. H. H. Hodgson and P. Anderson (*J. Chem. Soc.*, 1924, 125, 2195—2196).—4-Chloro-2-nitrotoluene and 4-chloro-3-nitrotoluene, obtained on nitrating *p*-chlorotoluene under various conditions (or by the Sandmeyer reaction from the corresponding nitrotoluidines), are quantitatively converted into 4-chloro-*o*-toluidine (I) and 3-amino-*p*-tolyl mercaptan (II), respectively, by boiling with sodium di- or tri-sulphide in alcoholic solution. The quantities of I and II in the reduction product are found: (*a*) by titration of each after separation by steam distillation; (*b*) by diazotisation, when II is converted into the insoluble diazosulphide, $C_7H_6{<}\begin{matrix}N_2\\|\\S\end{matrix}$, whilst diazotised I is coupled with β-naphthol and the azo compound weighed. The figures obtained by this method of analysis agree very closely with those calculated by interpolation and extrapolation of Holleman's cryoscopic data (A., 1909, i, 18). A. C.

Ammonium as a Reducing Agent. H. H. SCHLUBACH and H. MIEDEL (*Ber.*, 1924, **57**, [*B*], 1682—1686).—A solution of sodium in liquid ammonia is added gradually to a solution of ammonium chloride in the same solvent in which the substance to be reduced is at least partly dissolved at —80° to —50°. If the compound under investigation is not sufficiently soluble in liquid ammonia, benzene or ether may be added. In general, reduction appears to be due to the direct addition of nascent hydrogen without preliminary formation of an intermediate additive compound with the sodium. The action is highly selective and appears to resemble most closely that of sodium and alcohol. Probably owing to the low temperature of the reactions, the formation of by-products is largely avoided.

Phenylbutylene is smoothly hydrogenated to phenylbutane, whereas cinnamic acid and stilbene remain unchanged. Benzophenone is converted directly into diphenylmethane; the intermediate production of benzhydrol could not be established. On the other hand, Michler's ketone, didiphenylyl ketone, benzil, benzoin, and deoxybenzoin are unaffected. Acetophenone could not be reduced, whereas β-phenylethyl methyl ketone readily yields α-phenylbutan-γ-ol. The latter substance is also obtained with rather greater difficulty from styryl methyl ketone. Less favourable results were obtained with 1 : 3-dimethyl-Δ^6-*cyclo*hexen-5-one and methylheptenone. Benzene is unaffected, whereas pyridine is converted into piperidine. Nitrobenzene is transformed into aniline. H. W.

Synthesis of Diaryl Compounds by means of the Diazo Reaction. M. GOMBERG and W. E. BACHMANN (*J. Amer. Chem. Soc.*, 1924, **46**, 2339—2343).—In the formation of diaryl compounds by Bamberger's method (A., 1896, i, 299) the isolation of the unstable explosive diazonium oxides (or diazo anhydrides) is unnecessary. Both symmetrical and unsymmetrical diaryl compounds may be obtained by diazotising the amine in the usual manner, adding the hydrocarbon, and slowly adding to the cooled, well-stirred mixture a 15 to 25% sodium hydroxide solution until the mixture contains about 1 to 2% of free alkali. Equally good results were obtained by adding benzenediazonium chloride to a well-stirred mixture of benzene and sodium hydroxide solution, the solution at the end containing 2% of free alkali. It is suggested that the normal sodium diazotate is first produced and that this undergoes partial hydrolysis: $2RN_2{\cdot}ONa+2H_2O \rightleftharpoons 2RN_2{\cdot}OH+2NaOH$; $2RN_2{\cdot}OH \rightleftharpoons RN_2{\cdot}O{\cdot}N_2R+H_2O$. With benzene and benzenediazonium chloride, in addition to diphenyl, *p*-phenyldiphenyl and more complex products are produced by the diazo compound coupling with the diaryl compound first formed (cf. Gerngross and Dunkel, this vol., i, 720).

The following compounds have been prepared by this method (the figures in brackets denote yields in % of theory): From aniline, diphenyl (22%), phenylthiophen (11%), *p*-cyanodiphenyl (10%), *o*- and *p*-bromodiphenyl, methyl diphenyl-4-carboxylate, *p*-nitrodiphenyl, and phenylpyridine. From *p*-bromoaniline, *p*-bromodiphenyl (40—46%), p-*bromophenylthiophen*, m. p. 100° (20%); from *m*-bromoaniline, m-*bromodiphenyl*, b. p. 299—301° (28%); from *p*-chloroaniline, *p*-chlorodiphenyl (41%), p-*chlorophenylthiophen*, m. p. 83° (24%); from *m*-chloroaniline, m-*chlorodiphenyl*, b. p. 284—285° (27%); from *p*-nitroaniline, *p*-nitrodiphenyl (30%), p-*nitrophenylthiophen*, m. p. 137—138° (23%); from *m*-nitroaniline, *m*-nitrodiphenyl (18%); from *o*-nitroaniline, *o*-nitrodiphenyl; from *p*-cyanoaniline, *p*-cyanodiphenyl (15%); from *m*-cyanoaniline, m-*cyanodiphenyl*, m. p. 49° (19%), m-*cyanophenylthiophen*, m. p. 53—54° (15%); from *p*-aminodiphenyl, *p*-phenyldiphenyl; and from ethyl *p*-aminobenzoate, ethyl diphenyl-4-carboxylate (12%).

R. B.

Action of Nitric Acid on αα-Diphenylethylene and αα-Di-*p*-tolylethylene. II. R. Anschütz and A. Hilbert (*Ber.*, 1924, **57**, [*B*], 1697—1700; cf. Anschütz and Hilbert, A., 1921, i, 783; Konovalov and Jatzewitsch, A., 1905, i, 763).—β-Nitro-αα-diphenylethyl alcohol is converted by reduction with granulated zinc and glacial acetic acid into β-amino-αα-diphenylethyl alcohol, m. p. 110°, whereas stannous chloride transforms it into benzophenone and methylamine. β-Nitro-α-ethoxy-αα-diphenylethane, m. p. 91—92° (cf. Konovalov and Jatzewitsch, *loc. cit.*), and β-*nitro-α-methoxy-αα-diphenylethane*, m. p. 139°, are described. Di-*p*-tolylethylene, b. p. 163—165°/13 mm., m. p. 61°, is prepared by the action of magnesium *p*-tolyl bromide on ethyl acetate and subsequent distillation of the product. It is converted by bromine in carbon disulphide solution into β-*bromo-αα-di*-p-*tolylethylene*, m. p. 67°, and is reduced by sodium and alcohol to αα-di-*p*-tolylethane, b. p. 155—157°/12 mm. The hydrocarbons are converted by nitric acid in glacial acetic acid solution into β-*nitro-αα-di*-p-*tolylethylene*, m. p. 116°, which is oxidised by chromic acid to di-*p*-tolyl ketone. p-*Nitro-α-ethoxy-αα-di*-p-*tolylethane*, prepared by the action of sodium ethoxide on β-nitro-αα-di-*p*-tolylethylene, has m. p. 95°.

H. W.

Partition of Silver Nitrate between Aniline and Water. A. Frumkin and R. Kulvarskaja.—(See ii, 757.)

Action of Aromatic Amines on Semicarbazide Hydrochloride. H. Mazourewitch (*Bull. Soc. chim.*, 1924, [iv], **35**, 1183—1186).—The *s*-diphenylcarbamide formed as a by-product in the action of aniline on the semicarbazidesemicarbazones of mesityl oxide and 3-methyl-5-ethyl-Δ^2-*cyclo*hexenone (this vol., i, 969) probably results from the decomposition of the semicarbazidesemicarbazones, since it is now shown that the action of boiling aromatic amines on semicarbazide hydrochloride yields the corresponding substituted carbamide, the suggested mechanism of the reaction being as follows: $R{\cdot}NH_2+NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2=NH_2{\cdot}NH{\cdot}CO{\cdot}NHR+NH_3$; $NH_2{\cdot}NH{\cdot}CO{\cdot}NHR+NH_2R=(NHR)_2CO+(NH_2)_2$. Thus aniline and semicarbazide hydrochloride yield *s*-diphenylcarbamide, m. p. 233—235° (decomp.); similarly, *o*-toluidine yields *s*-di-*o*-tolylcarbamide, m. p. 237—239° (decomp.); *p*-toluidine, *s*-di-*p*-tolylcarbamide, m. p. 248—253° (decomp.); 3-*o*-xylidine, *s*-di-*o*-xylylcarbamide, m. p. 242° (decomp.), and benzylamine, *s*-dibenzylcarbamide, m. p. 168°. With *p*-aminoacetophenone and *p*-bromoaniline, the reaction is more complicated and definite products have not been isolated. R. B.

Velocity of Benzylation of certain Amines. D. H. Peacock (*J. Chem. Soc.*, 1924, **125**, 1975—1980).—Aniline and other amines have been benzylated by means of benzyl chloride and *p*-nitrobenzyl chloride and the reaction velocity constants determined from the expression used by Menschutkin (cf. A., 1890, 1366; 1900, 335) and also from an amended expression which takes into account the action of amine on the hydrochloride formed. Both equations give similar results for the initial stages, but that of Menschutkin agrees better with the later stages in spite of the above consideration. The following values were found for k_{35}, k_{45}, and E (the energy of activation): Aniline–benzyl chloride, 0·00157, 0·00315, 13454 cal.; aniline–*p*-nitrobenzyl chloride, 0·000588, 0·00125, 14678 cal.; *p*-toluidine–benzyl chloride, 0·00217, 0·00495, 16050 cal.; *p*-toluidine–*p*-nitrobenzyl chloride, 0·00137, 0·00252, 11860 cal. The value E is calculated from $\log k_1/k_2=E/R(1/T_2-1/T_1)$. The value of the velocity coefficients changes with the concentration of the reactants and particularly of the amine. Values of k are given for the reaction of 9 bases with benzyl chloride in alcohol at 40°. The following benzylated amines and their benzoyl (A) and *p*-toluenesulphonyl (B) derivatives were isolated: *Benzyl*-o-*chloroaniline*, m. p. 44°, (A) m. p. 111°; *benzyl*-p-*chloroaniline*, m. p. 45°, (A) m. p. 138°; *benzyl*-2 : 5-*dichloroaniline*, m. p. 47°, (A) m. p. 69°; *benzylaniline*, (A) m. p. 105°, (B) m. p. 133°; *benzyl*-o-*toluidine*, (A) m. p. 65°; *benzyl*-p-*toluidine*, (A) m. p. 127°, (B) m. p. 126°. A. C.

Chlorine or Bromine Derivatives obtained by the Aid of Mixtures of Hydrogen Peroxide and the Corresponding Halogen Acids. A. Leulier (*Bull. Soc. chim.*, 1924, [iv], **35**, 1325—1330).—A mixture of hydrogen peroxide and hydrochloric or hydrobromic acid is a satisfactory source of nascent halogen for the preparation of aromatic bromo or chloro derivatives.

The following compounds were prepared in this way: *p*-Chloroacetanilide (poor yield), 3 : 5-dichloro-*o*-nitroaniline, 2 : 6-dichloro-*p*-nitroaniline (74% yield), a *chloro*-2 : 4-*dinitroaniline* (m. p. 131—132°), 5-chloroaceto-*o*-toluidide (poor yield), 3-chloro-5-nitro-*o*-toluidine, chloroaceto-*p*-phenetidide (m. p. 123—124°), 5-bromoaceto-*o*-toluidide, 3-bromo-5-nitro-*o*-toluidine. Brominations proceed more satisfactorily than chlorinations. W. E. E.

Magnesium Anilide. A. TERENTIEFF (*Bull. Soc. chim.*, 1924, [iv], 35, 1164—1168).—In the absence of air, magnesium reacts with aniline vapour at 370—380° under atmospheric pressure, yielding magnesium anilide, $(NHPh)_2Mg$, a light yellow powder. The product is unstable in air and rapidly blackens; its composition was accordingly calculated from the amounts of aniline consumed and of hydrogen liberated out of contact with air. Magnesium anilide is violently decomposed by water with regeneration of aniline (cf. Meunier, A., 1903, i, 544); alcohol vapour at 100—110° causes a similar decomposition, yielding aniline. With ethyl acetate vapour at 200°, acetanilide is produced (cf. Bodroux, A., 1904, i, 662; 1905, i, 585). In a current of dry air at 100°, profound oxidation takes place, but a small quantity of azobenzene was the only product isolated; the reaction with oxygen is explosive. Carbon dioxide at 180° yields magnesium phenylcarbamate, $(NHPh\cdot CO_2)_2Mg$ (cf. Houben, A., 1904, i, 1104; 1909, i, 921), which on heating at 250—270° is decomposed into magnesium oxide, carbon dioxide, and *s*-diphenylcarbamide. R. B.

New Types of Ter- and Quadri-valent Compounds of Manganese. F. OLSSON (*Arkiv Kem., Min., Geol.*, 1924, 9, No. 10, 5—9).—When solutions of chlorides of organic bases in absolute alcohol, saturated with hydrogen chloride, are mixed with manganese trichloride solution obtained by reduction of potassium permanganate in alcoholic solution by means of hydrogen chloride (cf. Meyer and Best, A., 1900, ii, 77), double salts with chlorides of quaternary ammonium bases, $2RCl,MnCl_3$ (R=an organic base), are obtained. The formation of these compounds is probably determined by their low solubility in alcohol. Such pentachloromanganates are green and are free from solvent in the form of alcohol of crystallisation. The compounds prepared were: $(NMe_4)_2MnCl_5$; $(NEt_4)_2MnCl_5$; $(NPr_4)_2MnCl_5$; $(NPhMe_3)_2MnCl_5$; $(NPhEt_3)_2MnCl_5$; $(NPhMe_2Et)_2MnCl_5$; $(NPhMeEt_2)_2MnCl_5$; $(NHMe_3Et)_2MnCl_5$; $(NMe\cdot C_{10}H_8Me)_2MnCl_5$; $(NEt\cdot C_{10}H_8Me)_2MnCl_5$; $(NMe_3\cdot C_6H_4Me)_2MnCl_5$; $(NPhMeEtPr)_2MnCl_5$. When the compound $NEt_4\cdot MnO_4$, obtained from silver permanganate and tetraethylammonium chloride, is reduced by acetic acid and dry hydrogen chloride is passed through the solution, the reddish-brown *compound*, $NEt_4\cdot MnCl_4,2C_2H_4O_2$, gradually separates.

The double iodates, $K(Rb,Cs,NH_4)_2Mn(IO_3)_5$, prepared by the action of the alkali iodates on the compound $Mn(OAc)_3,2H_2O,HIO_3$, crystallise in yellow or yellowish-brown, doubly-refracting, cube-like octahedra, and are more stable in the air and towards the usual reagents than the double chlorides.

The following periodates of tervalent manganese,
$(M''O,Mn_2O_3,I_2O_7,xH_2O)$,
prepared by Price's method (A., 1903, ii, 652), form red crystals, but turn brown at 110°, with loss of their water of crystallisation: $M=H_2$, $x=5$; $M=Na_2$, $x=3$; $M=K_2$, $x=2$; $M=Sr$, $x=3$; $M=Mg$, $x=3$; $M=(CH_6N_3)_2$, $x=8$; $M=Ag_2$, $x=0$; $M=Cd$, $x=4$; $M=Zn$, $x=4$; $M=Cu$, $x=3$; $M=Pb$, $x=3$.

The *compound* $Mn(CHBzAc)_3$, prepared from benzoylacetone and manganese acetate, forms microscopic, stellar aggregates of green prisms, m. p. 168·5°.

By the action of manganese tetrachloride, prepared by Weinland and Dinkelacker's method (A., 1909, ii, 48), on different chlorides at the temperature of solid carbon dioxide, the following double chlorides are obtained as black crystals: $(NMe_4)_2MnCl_6$; $(NPhMe_3)_2MnCl_6$; $(NMe_3\cdot C_6H_4Me)_2MnCl_6$; $(NPhMe_2Et)_2MnCl_6$; $(NPhMeEt_2)_2MnCl_6$. Double iodates of quadrivalent manganese having the formulæ $Rb_2Mn(IO_3)_6$ and $Cs_2Mn(IO_3)_6$ are obtainable by the action of iodic acid and alkali iodate on manganese dioxide suspended in water (cf. Berg, A., 1899, ii, 426). The corresponding barium salt, described by Berg, is obtainable more readily by dissolving manganese triacetate, barium iodate, and iodic acid in 10% nitric acid.

Periodates of quadrivalent manganese $(M''O,2MnO_2,I_2O_7,xH_2O)$ may be obtained as crystalline powders by the interaction of manganic acetate, 10% nitric acid, and periodates. The following were prepared: $M=H_2$, $x=5$; $M=Na_2$, $x=2$; $M=K_2$, $x=1·5$; $M=Ca$, $x=4$; $M=Sr$, $x=4$; $M=Mg$, $x=3$; $M=Ag_2$, $x=2$; $M=(CH_6N_3)_2$, $x=10$; $M=Cd$, $x=5$; $M=Zn$, $x=3·5$; $M=Cu$, $x=4$; $M=Pb$, $x=2$; also $Al_2O_3,4MnO_2,2I_2O_7,10H_2O$. T. H. P.

Quinquevalent Chromium. F. OLSSON (*Arkiv Kem., Min., Geol.*, 1924, 9, No. 10, 10—12).—The addition to a solution of chromium oxychloride of chlorides of organic bases dissolved in concentrated acetic acid saturated with hydrogen chloride (cf. Weinland and Fiederer, A., 1907, i, 549; ii, 31) yields double chlorides of the form $RCl,CrOCl_3$; variation of the proportions of the reagents within wide limits is without influence on the composition of the resulting compounds, which form reddish- or yellowish-brown, rhombic tablets and are moderately stable in dry air. Such are: NMe_4CrOCl_4; NEt_4CrOCl_4; NPr_4CrOCl_4; $NPhMe_3CrOCl_4$; $NPhEt_3CrOCl_4$; $NPhMe_2EtCrOCl_4$; $NPhMeEt_2CrOCl_4$; $NMe(C_{10}H_8Me)\cdot CrOCl_4$; $NEt(C_{10}H_8Me)\cdot CrOCl_4$; $NMe_3(C_6H_4Me)\cdot CrOCl_4$; $NPhMeEtPrCrOCl_4$.

Addition of an aqueous solution of the compound $4CrO_3,Cr_2O_3$ to excess of a solution of potassium fluoride in 40% hydrofluoric acid at 0° yields the compound KF,CrO_2F,H_2O as a yellowish-brown precipitate. T. H. P.

Stereochemistry of Saturated Tervalent Nitrogen. VI. Attempts to Prepare Optically Active Compounds of Tervalent Nitrogen. J. MEISENHEIMER, L. ANGERMANN, O. FINN, and E. VIEWEG (*Ber.*, 1924, 57, [*B*], 1744—1759).—Although the existence of an asymmetric, saturated, tervalent nitrogen atom has frequently been assumed in order to account for the formation of stereoisomeric compounds containing this atom, no substance of this class has hitherto been resolved into optically active components. With this end in view, a large number of tertiary amines, particularly such as contain the acetonyl and phenacyl groups, which appear to exert a favourable influence on the resolution of sulphonium compounds, have been examined with entirely negative results. It is therefore concluded that saturated, tervalent nitrogen, unless present in a particular manner in a polycyclic ring system, seldom if ever causes the phenomenon of stereoisomerism; this conclusion is in harmony with the observations of Pope and his co-workers (T., 1904, **85**, 1330; 1907, **91**, 458; 1910, **97**, 2199). The attribution of the non-resolvability of these compounds to the presence of the three radicals attached to the nitrogen atom in the same plane as the nitrogen atom involves difficulties in other directions, so that it is assumed that this is only a mean position around which the atoms in ammonia and the amines constantly oscillate. Stabilisation occurs only when the fourth co-ordination position of the nitrogen atom is occupied by a positively charged hydrogen atom or an alkyl residue (ammonium compounds), an oxygen atom (amine oxides), or a complex metallic residue (ammines). According to Werner's theory, a close analogy exists between the amines and the ions of sulphonium salts, [Sabc]X. Since, however, the former are non-resolvable whereas the latter have been resolved, this analogy cannot be fully maintained. It appears more probable that the central sulphur atom is co-ordinatively quadrivalent and that when sulphonium salts become ionised the tetrahedral disposition of the radicals is maintained by the immediate substitution of water for halogen: $\left[\begin{matrix}\mathrm{Me} & & \mathrm{Me} \\ & \mathrm{S} & \\ \mathrm{Me} & & \mathrm{Cl}\end{matrix}\right] \xrightarrow[\text{in water}]{\text{solution}} \left[\begin{matrix}\mathrm{Me} & & \mathrm{Me} \\ & \mathrm{S} & \\ \mathrm{Me} & & \mathrm{Aq}\end{matrix}\right]\mathrm{Cl}$.

1-*Methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* d-π-*bromocamphorsulphonate*, $C_{10}H_{12}N{\cdot}C_{10}H_{15}O_4BrS$, prepared from its components in ethyl acetate, has m. p. 141° (decomp.), $[M]_D$ +276° in ethyl alcohol; the corresponding *monohydrate* has m. p. 137°. Diethylaniline gives a d-π-*bromocamphorsulphonate*, m. p. 222—223°, $[M]_D$ +272° in alcohol. Ethylaniline gave with a somewhat old specimen of the acid mainly *ethylaniline* d-π-*bromocamphorsulphonate*, m. p. 146·5—148° (*monohydrate*, m. p. about 80°), together with smaller amounts of a *salt*, $C_8H_{11}N,C_{16}H_{10}O_4BrS$, m. p. 195—196°, which is probably derived from *d-iso*bromocamphorsulphonic acid (cf. Kipping, T., 1905, **87**, 635). *Ethylpropylaniline* d-π-*bromocamphorsulphonate* has m. p. 137—138°.

Acetonylmethylethylamine, $C_6H_{13}ON$, an unstable liquid, b. p. 44—45°/15 mm., prepared from methylethylamine and chloroacetone in ethereal solution, yields a *picrate*, m. p. indefinite, 80—85°, and a d-α-*bromocamphor*-π-*sulphonate*, m. p. 115—122°, $[M]_D$ +275°. *Phenacylmethylethylamine*, b. p. 130—131°/11 mm., the *picrate*, m. p. 116—118° after previous softening, and the d-*bromocamphorsulphonate*, m. p. 141—142° after softening at 137°, $[M]_D$

+276°, are described. Methylaniline and chloroacetone give a mixture of 1 : 3-*dimethylindole*, b. p. 119—120°/7 mm. (*picrate*, m. p. 141—143°), much unchanged methylaniline, and *acetonylmethylaniline*, b. p. 135—136°/8 mm.; the latter substance yields a crystalline *picrate*, but its salts with optically active acids could not be caused to crystallise. 1-*Acetonyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, b. p. 178°/17 mm., m. p. 39—41°, gives a d-*bromocamphorsulphonate*, m. p. (indefinite) 110—116°, $[M]_D$ +265°. 1-*Phenacyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 101—103°, and its d-*bromocamphorsulphonate*, m. p. (indefinite) 110—135°, are described; the base recovered from the salt was optically inactive. *Acetonylmethyl*cyclo*hexylamine*, b. p. 106°/11 mm., does not yield a crystalline bromocamphorsulphonate; the *picrate* has m. p. 162—163° after previous softening. The amine absorbs oxygen when dissolved in ether and becomes converted into *benzoylmethyl*cyclo*hexylamine*, m. p. 130—135°.

N-*Phenyl*-N-p-*tolylanthranilic acid*, m. p. 173°, prepared from phenylanthranilic acid, *p*-iodotoluene, copper powder, and potassium carbonate in the presence of nitrobenzene at 200—215°, is readily purified through the sparingly soluble, tetrahydrated *sodium* salt; it could not be resolved by means of the *strychnine* salt, m. p. 184—185°, or *quinine* salt (+C_6H_6), m. p. 154—164°; the cinchonine, brucine, and morphine salts do not crystallise satisfactorily. *Phenyl-α-naphthylanthranilic acid*, m. p. 226°, could not be resolved by means of its *brucine* salt (+1·5H_2O), m. p. 237°, or *morphine* salt (+4H_2O), m. p. 174° (decomp.) after softening at 155°. H. W.

Derivatives of Diphenylamine. E. PAPASOGLI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 106—110).—p-*Bromo*-p′-*nitrodiphenylamine*, $C_6H_4Br·NH·C_6H_4·NO_2$, prepared by treating *p*-nitrodiphenylamine with a mixture of sulphuric acid, bromine, and pyridine (or quinoline) in acetic acid solution, forms orange-yellow crystals, m. p. 162°. When subjected in acetic acid solution to a current of nitrous anhydride, it is converted into the required *nitrosoamine*, $C_6H_4Br·N(NO)·C_6H_4·NO_2$, m. p. 151°, which yields *p*-bromo-*p*′-nitrodiphenylamine when treated with hydroxylamine hydrochloride in alcoholic solution. T. H. P.

Derivatives of *ac*-Tetrahydro-β-naphthylamine. A. WINDAUS [with O. DALMER, H. SCHREITERER, R. HUPE, and H. KÖCHER] (*Ber.*, 1924, **57**, [*B*], 1731—1739).—2-Amino-7-hydroxynaphthalene is reduced by sodium and amyl alcohol to a mixture of 2-*amino*-7-*hydroxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 168·5°, and 2-*amino*-7-*hydroxy*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, which can be separated from one another, since only the former is soluble in sodium hydroxide solution; it yields a *hydrochloride*, m. p. 166·5°, a *picrate*, m. p. 205° after softening, and a *dibenzoyl* derivative, m. p. 174° after softening; 2-*acetamido*-7-*hydroxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene* has m. p. 195°. The base is converted by bromine in glacial acetic acid solution into 6 : 8-*dibromo*-2-*amino*-7-*hydroxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 251° (decomp.), after darkening at 215° (*hydrobromide*, m. p. 284°; *diacetyl* derivative, m. p. 187°). The action of nitric acid on a solution of 2-amino-7-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene in glacial acetic acid leads to the almost immediate separation of the *nitrate* of nitro-2-amino-7-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene; the corresponding free *base*, m. p. 236° (decomp.), its *hydrochloride*, decomp. 260—310°, and *diacetyl* derivative, m. p. 178°, are described. The filtrates from the nitrate described above gradually deposit the nitrate of 6 : 8-dinitro-2-amino-7-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene; the free *base*, m. p. 243° (decomp.), the *hydrochloride*, decomp. 220—290°, and the *diacetyl* derivative, m. p. 193° (decomp.), are described. The portion of the product of the reduction of 2-amino-7-hydroxynaphthalene which does not dissolve in sodium hydroxide (see above) is separated by light petroleum into 2-amino-7-hydroxy-5 : 6 : 7 : 8-tetrahydronaphthalene, m. p. 141·5°, b. p. 200—210°/12·5 mm. (*hydrochloride*, m. p. 236°; *picrate*, m. p. 181°), and ar-2-*aminodihydronaphthalene*, b. p. 150—155°/14 mm., m. p. 53° (*picrate*, m. p. 194° [decomp.]; *dibromo* compound, $C_{10}H_{11}NBr_2$, m. p. 62°); the *picrate* of *ar*-2-amino-tetrahydronaphthalene has m. p. 204° (decomp.).

2-*Amino-7-methoxynaphthalene*, m. p. 143° (*hydrochloride*, m. p. 222—223° [decomp.]; *picrate*, decomp. 165°; *acetyl* derivative, m. p. 156°), is prepared by the action of ammonium sulphite and ammonia on 2-hydroxy-7-methoxynaphthalene at 150—160°. It is reduced by sodium and boiling amyl alcohol to a mixture of the corresponding tetrahydro derivatives, which is separated into its components by treatment of its ethereal solution with carbon dioxide, whereby 2-amino-7-methoxy-1 : 2 : 3 : 4-tetrahydronaphthalene is precipitated as the *carbonate* (? *carbamate*); the free *base*, a colourless liquid, *hydrochloride*, m. p. 213°, *picrate*, decomp. about 212° after softening, and *picrolonate*, decomp. about 252°, are described. The base is converted by hydriodic acid into 2-amino-7-hydroxy-1:2:3:4-tetrahydronaphthalene. The physical constants of the *hydrochloride*, m. p. 225°, *picrate*, m. p. 183° (decomp.), and *acetyl* derivative, m. p. 93°, of 2-amino-7-methoxy-5 : 6 : 7 : 8-tetrahydronaphthalene, are given with reserve as the complete freedom of the base from the isomeric 1 : 2 : 3 : 4-tetrahydro compound is not established. 2-*Hydroxy-7-methoxy-*1 : 2 : 3 : 4-*tetrahydronaphthalene*, prepared by the catalytic hydrogenation of 2-hydroxy-7-methoxynaphthalene in the presence of spongy palladium, has m. p. 71°.

2 : 7-Diaminonaphthalene (*dipicrate*, m. p. 210°; *diacetyl* derivative, m. p. 261°; *dibenzoyl* derivative, m. p. 267°) is reduced by sodium and boiling amyl alcohol to 2 : 7-*diamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 162°/20 mm., m. p. about 60° (*hydrochloride*, m. p. about 360° [decomp.]; *diacetyl* derivative, m. p. 203°; *dibenzoyl* compound, m. p. 255°). It is transformed by nitrous acid into 2-amino-7-hydroxy-1 : 2 : 3 : 4-tetrahydronaphthalene.

The following derivatives of 2 : 6-dihydroxynaphthalene are described: the *monomethyl ether*, m. p. 136—137°; 2-*amino-*

6-*methoxynaphthalene*, m. p. 139—140° (*hydrochloride*, m. p. 181°; *acetyl* derivative, m. p. 159—160°). 2 : 6-*Diaminonaphthalene*, m. p. 216—217°, is smoothly reduced to 2 : 6-*diamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 61°; the *hydrochloride*, diacetyl derivative, m. p. 240°, and *dibenzoyl* compound, m. p. 258°, are described. H. W.

Nitrophenyl Ethers and their Halogen Substitution Products. O. Matter (D.R.-P. 386618; from *Chem. Zentr.*, 1924, i, 2632).—Nitrophenyl ethers are prepared by heating mono- or poly-halogenated nitrohydrocarbons with monohydric alcohols and feebly basic metal hydroxides, carbonates, or hydrogen carbonates, with or without the addition of catalysts. For example, *p*-chloronitrobenzene yields *p*-nitroanisole on heating at 175—185° with sodium carbonate and diluted methyl alcohol; at 200—210° with sodium carbonate, ethyl alcohol, and copper powder, *p*-nitrophenetole is formed. With slight variations in the conditions 3 : 4-dichloronitrobenzene yields 2-chloro-4-nitroanisole, m. p. 95°, and 2 : 5-dichloronitrobenzene yields 4-chloro-2-nitroanisole, m. p. 95°, and 4-chloro-2-nitrophenetole, m. p. 61—62°. F. A. M.

Solubility and Partition Measurements of Picric Acid in Solutions of Salts. E. Schreiner (*Z. anorg. Chem.*, 1924, **138**, 311—321).—By means of measurements of conductivity and catalytic power, the value $K_0=0{\cdot}31$ at 25° is found for the dissociation constant of picric acid in water on the basis of Bjerrum's theory (A., 1919, ii, 9); a closely agreeing value is given by *E.M.F.* measurements. The solubility of picric acid in water at 25° is $c_0=0{\cdot}0575$ mol. per litre, and its solubility has been measured in aqueous solutions of sodium chloride, barium chloride, and magnesium sulphate. The partition of picric acid between benzene and aqueous solutions of the above-mentioned salts has also been studied, and the hydrogen-ion concentration calculated in each case. The experimental results together with those of Rothmund and Drucker (A., 1904, ii, 391) are used to calculate the partition and solubility constants on the basis of Bjerrum's theory, and satisfactorily constant values are obtained. W. H.-R.

Steric Hindrance in the Migration of Acyl from Nitrogen to Oxygen. L. C. Raiford and C. M. Woolfolk (*J. Amer. Chem. Soc.*, 1924, **46**, 2246—2255).—The migration of the acetyl group from nitrogen to oxygen when an *o*-acetamidophenol is benzoylated by the Schotten–Baumann method (A., 1923, i, 326) is not inhibited by the presence of bromine atoms ortho to the amino and hydroxyl groups, although in the case of 2 : 5 : 6-tribromo-3-acetamido-*p*-cresol either benzoylation was incomplete or migration was only partial.

2 : 3 : 5-Tribromo-*p*-cresol, m. p. 99°, on treatment with sodium nitrite and glacial acetic acid, is converted into 2 : 5-dibromo-3-nitro-*p*-cresol (or 5 : 6-dibromo-3-nitro-*p*-cresol), m. p. 123°, which is reduced by Raiford's method (A., 1911, i, 993) to the corresponding 2 : 5(or 5 : 6)-dibromo-3-amino-*p*-cresol, m. p. 122°.

Acetic anhydride and sodium acetate convert the base into 2 : 5 (or 5 : 6)-*dibromo-3-acetamido-*p*-tolyl acetate*, needles, hydrolysed by 10% aqueous sodium hydroxide to 2 : 5(or 5 : 6)-*dibromo-3-acetamido-*p*-cresol*, m. p. 158°, which with benzoyl chloride and sodium hydroxide gives, in 77% yield, 2 : 5(or 5 : 6)-*dibromo-3-benzoylamido-*p*-tolyl acetate*, m. p. 232°, hydrolysed by methyl-alcoholic sodium hydroxide to 2 : 5(or 5 : 6)-*dibromo-3-benzoylamido-*p*-cresol*, m. p. 154° (decomp.). The latter compound is identical with that obtained by benzoylating 2 : 5(or 5 : 6)-dibromo-3-amino-*p*-cresol by Ransom's method (A., i, 1900, 218) and on acetylation is converted into the benzoylamido-*p*-tolyl acetate.

Acetylation of 2 : 5 : 6-*tribromo-3-amino-*p*-cresol* with sodium acetate and acetic anhydride gives in 92% yield slightly impure 2 : 5 : 6-*tribromo-3-acetamido-*p*-tolyl acetate*, m. p. 171°, which on hydrolysis with 1% sodium hydroxide yields 2 : 5 : 6-*tribromo-3-acetamido-*p*-cresol*, m. p. 189°. Benzoyl chloride and sodium hydroxide convert this into 2 : 5 : 6-*tribromo-3-benzoylamido-*p*-tolyl acetate*, m. p. 177° (blackening) (yield 72%), the structure of which follows from its hydrolysis with aqueous alcoholic sodium hydroxide to 2 : 5 : 6-*tribromo-3-benzoylamido-*p*-cresol*, m. p. 195°, identical with the product obtained by benzoylating 2 : 5 : 6-tribromo-3-amino-*p*-cresol by Ransom's method. Acetic anhydride and sodium acetate convert the benzoylamido-*p*-cresol into the *p*-tolyl acetate, m. p. 195°.

Tetrabromo-*o*-cresol, m. p. 204°, on treatment with sodium nitrite and acetic acid, gives in addition to the 4 : 5 : 6-tribromo-3-nitro-*o*-cresol, m. p. 159°, the isomeric 3 : 4 : 6-tribromo-5-nitro-*o*-cresol, m. p. 177° (decomp.), obtained by Zincke and Klostermann (A., 1907, i, 322). On reduction by Raiford's method, the 4 : 5 : 6-tribromo derivative gives, in 74% yield, the *hydrochloride* of 4 : 5 : 6-*tribromo-3-amino-*o*-cresol*; the free *base* has m. p. 167°. Acetylation of the base by the usual method gives, in 86% yield, 4 : 5 : 6-*tribromo-3-acetamido-*o*-tolyl acetate*, m. p. 146°, which on hydrolysis with aqueous alcoholic alkali gives an 82% yield of 4 : 5 : 6-*tribromo-3-acetamido-*o*-cresol*, m. p. 186°. Benzoylation converts the last into 4 : 5 : 6-*tribromo-3-benzoylamido-*o*-tolyl acetate*, m. p. 234°, the structure of which is established by its synthesis by benzoylation of 4 : 5 : 6-tribromo-3-amino-*o*-cresol by Ransom's method, followed by acetylation of the 4 : 5 : 6-*tribromo-3-benzoylamido-*o*-cresol*, m. p. 133°, with sodium acetate and acetic anhydride. R. B.

Influence of Weight of Acyl in the Migration from Nitrogen to Oxygen. II. L. C. Raiford amd J. R. Couture (*J. Amer. Chem. Soc.*, 1924, 46, 2305—2318).—In continuation of their previous work on the migration of acetyl from nitrogen to oxygen in benzoylation by the Schotten–Baumann method (A., 1920, i, 156; 1922, i, 931; 1923, i, 326, 925), the authors have repeated the work of Auwers and Eisenlohr on acetylbenzoyl derivatives of 3-amino-*p*-cresol. Two different mixed diacyl derivatives were obtained, each of which gave a mixture of mono-*N*-acylated derivatives on hydrolysis. A study of the acylation of 5-bromo-3-amino-*p*-cresol and 4 : 6-dibromo-*o*-aminophenol shows that an increase in the weight of the aliphatic acyl radical hinders its displacement by benzoyl. The introduction of a nitro group into the benzoyl radical in the meta- or para-position greatly weakens the power of the radical to displace other groups from nitrogen in acylated *o*-aminophenols. The effect is greatest when the nitro group is in the para-position, but the introduction of a chlorine atom in the para-position does not diminish the power of the benzoyl group to displace other acyl groups. Neither relative weight nor relative acidity of the acyl radicals is the sole determining factor in the migration, and rearrangement may occur in both directions either in acylation or in hydrolysis. With two acyl groups of the same weight, one aromatic and one aliphatic, there is little tendency for replacement in acylation, but migration may occur during hydrolysis.

3-Acetamido-*p*-cresol, m. p. 158°, on benzoylation, yields 3-acetamido-*p*-tolyl benzoate, m. p. 147°; the isomeric 3-benzamido-*p*-tolyl acetate melts at 135°. 4 : 6-*Dibromo*-o-*propionamidophenyl propionate*, m. p. 162°, obtained on heating the hydrochloride of the base with sodium propionate and excess of propionic anhydride [the *tripropionyl* derivative, $C_3H_5O{\cdot}OC_6H_2Br_2{\cdot}N(C_3H_5O)_2$, m. p. 153°, is obtained with a large excess of anhydride], on hydrolysis with dilute alkali yields 4 : 6-*dibromo*-o-*propionamidophenol*, m. p. 88°, which on benzoylation gives in 99·4% a *propionylbenzoyl* derivative, m. p. 182°, identical with that obtained by the action of propionic anhydride on 4 : 6-dibromo-*o*-benzoylamidophenol, and yielding on hydrolysis a mixture of the *N*-benzoyl and *N*-propionyl compounds. 4 : 6-*Dibromo*-o-n-*hexoamidophenyl hexoate*, m. p. 111°, obtained by the action of *n*-hexoyl chloride on the phenol in pyridine, on hydrolysis yields 4 : 6-*dibromo*-o-*hexoamidophenol*, m. p. 70—71°, converted quantitatively by benzoyl chloride into 4 : 6-*dibromo*-o-*hexoamidophenyl benzoate*, m. p. 137°, hydrolysed to a mixture of *N*-benzoyl and *N*-hexoyl-4 : 6-dibromo-*o*-aminophenol. The isomeric 4 : 6-*dibromo*-o-*benzoylamidophenyl hexoate*, m. p. 137°, also yields a mixture of the two *N*-acyl derivatives on hydrolysis. Similarly, 4 : 6-*dibromo*-o-*acetamidophenyl hexoate*, m. p. 120°, obtained by the action of hexoyl chloride on *o*-acetamidophenol, and 4 : 6-*dibromo*-o-*hexoamidophenyl acetate*, m. p. 133°, similarly prepared from *o*-hexoamidophenol, both yield on hydrolysis a mixture of the two acylamidophenols. Acetylation of 5-bromo-3-amino-*p*-cresol with excess of acetic anhydride in pyridine gives a *triacetyl* derivative, m. p. 109°, $OAc{\cdot}C_6H_2Br(Me){\cdot}NAc_2$. The diacetyl derivative obtained with acetyl chloride yields on hydrolysis the *N*-acetyl derivative, which with *p*-nitrobenzoyl chloride in pyridine is quantitatively converted into 5-*bromo*-3-*acetamido*-p-*tolyl* p-*nitrobenzoate*, m. p. 206°, identical with the product obtained by the action of acetyl chloride on 5-*bromo*-3-p-*nitrobenzoylamido*-p-*cresol*, m. p. 190°, and yielding *p*-nitrobenzoic acid and the acetamidophenol on hydrolysis. *p*-Nitrobenzoyl chloride and 4 : 6-dibromo-*o*-benzoylamidophenol, and benzoyl chloride and 4 : 6-*dibromo*-p-*nitrobenzoylamidophenol*, m. p. 214°, obtained by hydrolysis of the diacyl compound, yield the same *benzoylnitrobenzoyl* derivative, m. p.

246°, which on hydrolysis yields *p*-nitrobenzoic acid and the benzoylamidophenol. Similarly, the same *acetyl*-m-*nitrobenzoyl* compound, m. p. 190°, was obtained by the action of *m*-nitrobenzoyl chloride on 5-bromo-3-acetamido-*p*-cresol and of acetyl chloride on 5-*bromo*-3-m-*nitrobenzoylamido*-p-*cresol*, m. p. 190°, the diacyl compound on hydrolysis yielding both possible acylaminophenols. 5-*Bromo*-3-p-*chlorobenzoylamido*-p-*cresol*, m. p. 166°, from hydrolysis of the diacyl derivative, with acetyl chloride, and 5-bromo-3-acetamido-*p*-cresol with *p*-chlorobenzoyl chloride, yield the same diacyl derivative, which on hydrolysis yields the *N*-*p*-chlorobenzoyl derivative, but no *p*-chlorobenzoic acid. Similarly, 4 : 6-*dibromo*-2-p-*chlorobenzoylamidophenol*, m. p. 209—210°, and *p*-nitrobenzoyl chloride yield a p-*chlorobenzoyl*-p-*nitrobenzoyl* derivative, m. p. 276°, identical with that obtained from 4 : 6-dibromo-2-*p*-nitrobenzoylamidophenol and *p*-chlorobenzoyl chloride. On hydrolysis, this yields only *p*-nitrobenzoic acid and the *N*-*p*-chlorobenzoyl derivative, m. p. 209—210°. R. B.

Nitration of Derivatives of *p*- and *m*-Aminophenols. F. Reverdin (*Bull. Soc. chim.*, 1924, [iv], **35**, 1168—1183).—A general survey of researches on the nitration of derivatives of *p*-aminophenol (A., 1905, i, 51, 430; 1906, i, 165, 748; 1907, i, 37, 695; 1909, i, 377, 913; 1910, i, 470; 1911, i, 37, 776; 1912, i, 182, 963; 1913, i, 850; 1922, i, 537; 1923, i, 320, 714; this vol., i, 727) and *m*-aminophenol (A., 1914, i, 166, 831, 954; 1915, i, 60, 524, 878; 1916, i, 141, 645). R. B.

Action of Formic Acid on Phenols and Propenyl Phenolic Ethers. L. S. Glichitch (*Bull. Soc. chim.*, 1924, [iv], **35**, 1160—1164).—Phenolic ethers containing a propenyl side-chain are converted by boiling with 90% formic acid into their dimeric forms, which are thus readily obtained pure (cf. Semmler, A., 1908, i, 664). Anethole is converted in this way into dianethole, m. p. 133·5—134° (cf. Orndorff, A., 1898, i, 129), *iso*eugenol into di*iso*eugenol, methyl*iso*eugenol into dimethyldi*iso*eugenol, m. p. 105·5—106° (cf. Széki, A., 1906, i, 660; Ciamician and Silber, A., 1909, i, 306), *iso*safrole into di*iso*safrole, m. p. 145—145·5°, whilst the isomeric allyl compounds, methylchavicol, eugenol, methyleugenol, and safrole, are unchanged. The crude dimethyldi*iso*eugenol melts at 89°, but no compound m. p. 96° could be isolated in the recrystallisations. R. B.

Pyrocatechol Compounds of Sexa- and Quinque-valent Molybdenum. R. Weinland and P. Huthmann (*Arch. Pharm.*, 1924, **262**, 329—343; cf. A., 1920, i, 40).—Among the compounds of pyrocatechol and molybdic acid are many containing one or two pyrocatechol residues per atom of molybdenum, *viz.*,

$$MoO_2(OH)\cdot O\cdot C_6H_4\cdot OX$$

and $MoO_2(O\cdot C_6H_4\cdot OX)_2$, (where $X{=}NH_4$ or an organic basic radical). It is possible to obtain a number of products containing a higher proportion of pyrocatechol, but it is now shown that in these only two pyrocatechol residues are attached to the molybdenum, forming a complex anion, the rest of the pyrocatechol being probably attached to the cation by a secondary valency. If the compounds with organic bases having more than two pyrocatechol residues per atom of molybdenum are recrystallised, they readily lose some of their pyrocatechol and finally a compound is obtained containing never less than two pyrocatechol residues. Ethylenediamine forms such a compound, containing five pyrocatechol residues, and three of these may be readily removed as above. Pyrocatechol compounds of quinquevalent molybdenum are all prepared from the green salt, $MoOCl_3,2NH_4Cl$. As this gives a hydroxide, $MoO(OH)_3$, it was expected that it would yield compounds with three pyrocatechol residues per atom of molybdenum, but none was obtained with more than two. The following new substances are described: *barium monopyrocatecholmolybdate*, $[MoO_3(O\cdot C_6H_4\cdot O)]_2H_2Ba,3H_2O$, prepared from the corresponding ammonium salt; the *mono*- and *di-guanidine* salts (which, like the other members of this series, may be prepared by the interaction of either ammonium molybdate or the trioxide MoO_3, pyrocatechol, and the appropriate base or its salts), $[MoO_3(O\cdot C_6H_4\cdot O)]H_2\cdot CH_5N_3$, and

$$[MoO_2(O\cdot C_6H_4\cdot O)_2]H_2(CH_5N_3)_2,C_6H_4(OH)_2;$$

the *ethylenediamine* salt,

$$[MoO_2(O\cdot C_6H_4\cdot O)_2]H_2,C_2H_8N_2,3C_6H_4(OH)_2,H_2O,$$

the *piperidine* salts, $2[MoO_3(O\cdot C_6H_4\cdot O)]H_2\cdot C_5H_{11}N,3H_2O$ and $[MoO_2(O\cdot C_6H_4\cdot O)_2]H_2(NH_3)\cdot(C_5H_{11}N),2H_2O$; the *piperazine* salts, $[MoO_2(O\cdot C_6H_4\cdot O)_2]H_2\cdot C_4H_{10}N_2$ (and its mono- and di-hydrates) and $[MoO_3(O\cdot C_6H_4\cdot O),MoO_2(O\cdot C_6H_4\cdot O)_2]H_4\cdot C_4H_{10}N_2,2H_2O$ (and the corresponding tetrahydrate). The following derivatives of quinquevalent molybdenum are described: *guanidine* salt,

$$[MoO_2(O\cdot C_6H_4\cdot O)(OH)]H_2\cdot(CH_5N_3)_2,1\tfrac{1}{2}H_2O;$$

pyridine salt,

$$[MoO_2(O\cdot C_6H_4\cdot O)(OH),MoO(O\cdot C_6H_4\cdot O)_2(OH)]H_4\cdot(C_5H_5N)_2;$$

piperazine salt, $[MoO(O\cdot C_6H_4\cdot O)_2(OH)]H_2\cdot C_4H_{10}N_2,H_2O$. B. F.

Preparation of Potassium Guaiacolsulphonate ("Thiocol"). A. Decio (*Boll. Chim. farm.*, 1924, **63**, 529—530).—Guaiacolsulphonic acid, prepared by the action of sulphuric acid on guaiacol, is converted, together with the excess of sulphuric acid, into calcium salt by neutralisation with calcium carbonate. Treatment of the mixed calcium salts with potassium carbonate converts the calcium guaiacolsulphonate into the corresponding potassium salt, the calcium carbonate formed and the calcium sulphate being then removed by filtration. [Cf. *B.*, 1924, 964.] T. H. P.

Electrolytic Introduction of Alkyl Groups. J. M. Nelson and A. M. Collins (*J. Amer. Chem. Soc.*, 1924, **46**, 2256—2267).—In the electrolysis of a mixture of benzaldehyde and ethyl iodide, saturated with tetraethylammonium iodide, *α-phenylpropyl ethyl ether*, CHPhEt·OEt, b. p. 85—90°/15 mm., having a characteristic, pleasant odour, is obtained. It is oxidised to propiophenone by potassium dichromate and sulphuric acid. The introduction of the two ethyl groups is analogous to the reduction of benzaldehyde to benzyl alcohol and to its conversion into α-phenylpropyl alcohol by the Grignard reaction. The introduction of alkyl groups appears to take place with difficulty and other reactions occur simultaneously. Part of the benzaldehyde undergoes reduction to *as*-diphenylethylene glycol, *s*-diphenylethylene glycol (hydrobenzoin), and stilbene, which, together with ethylene, a benzoate resembling ethyl benzoate, an iodide (giving with dimethylaniline a substance, m. p. 152°) similar to, but not identical with, benzyl iodide, and a residual tar, are all formed at the cathode. Hydrobenzoin is always formed even when benzoic acid and water are excluded and the electrolysis is conducted in an atmosphere of nitrogen, and its formation may possibly take place as indicated: $2CHPhO + 2EtI + 2e \longrightarrow [CHPh(OH)\cdot]_2 + 2C_2H_4 + 2I^-$, a reaction which is analogous to the reducing action of magnesium ethyl bromide (cf. Hess and Rheinboldt, A., 1921, i, 777). The yield of α-phenylpropyl ethyl ether is not affected by the presence of traces of benzoic acid, nor by the absence of a diaphragm.

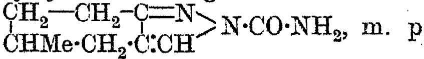
Preliminary experiments with benzaldehyde and methyl iodide indicate that a similar reaction obtains in this case, an *ether* which on oxidation yields acetophenone, and is probably α-phenylethyl methyl ether, being obtained. Attempts to introduce methyl groups into benzonitrile, propionitrile, and acetone by this method were unsuccessful, methane being formed practically in quantitative yield, calculated on the current consumption. R. B.

Utilisation of Cassia Oil for the Synthesis of Cinnamyl Alcohol. A. J. Hill and E. H. Nason (*J. Amer. Chem. Soc.*, 1924, **46**, 2236—2246).—The sodium hydrogen sulphite method of separating cinnamaldehyde from cassia oil is unsuitable for large-scale working (cf. Heusler, A., 1891, 1052; Tiemann, A., 1898, i, 247), but 85·7% of the theoretical yield can be separated as cinnamylidene diacetate by treatment of the oil with acetic anhydride in the presence of a few drops of sulphuric acid. The diacetate is readily hydrolysed to the aldehyde by heating with 10% sulphuric acid (yield 96%). On reduction of the diacetate with iron (8·3 mols.) and 50% acetic acid, yields of cinnamyl acetate up to 63·7% of theory (cf. Barbier and Leser, A., 1905, i, 653) are obtained in 12 hours. Large amounts of acetic acid retard the reduction. Copper sulphate inhibits the reduction, whilst nickel sulphate promotes the formation of phenylpropyl alcohol. With aluminium amalgam, reduction is incomplete; zinc–copper and zinc–nickel couples in alcoholic solution give hydrocinnamoin and other glycols (cf. Thiele, A., 1899, i, 616). Reduction with zinc and acetic acid gives similar results, cinnamyl acetate never being obtained when zinc is used. Cinnamyl acetate can also be obtained by reduction of cinnamaldehyde or cassia oil by the same method, the yield in the latter case being 77% of theory. Hydrolysis of the acetate with 5% alcoholic sodium hydroxide gives 96% of the theoretical yield of cinnamyl alcohol (p-*nitrobenzoate*, m. p. 78°), which is separated from any phenylpropyl alcohol by treatment with calcium chloride, with which the cinnamyl alcohol forms an additive compound. Cinnamaldehyde is best determined by precipitation of the phenylhydrazone in glacial acetic acid.

R. B.

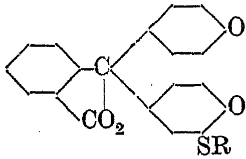
Molecular Transformations. XIV. Action of Acetyl Chloride on 4 : 4′ : 4″ : 4‴-Tetrabromobenzopinacone. Contribution to the Problem of Affinity. P. J. MONTAGNE (*Rec. trav. chim.*, 1924, **43**, 636—642; cf. *Ber.*, 1918, **51**, 1479).—The action of acetyl chloride on 4 : 4′ : 4″ : 4‴-tetrabromobenzopinacone simultaneously follows two courses. The main reaction results in the formation of 4 : 4′ : 4″ : 4‴-tetrabromobenzopinacolin, whilst the side reaction gives 4 : 4′-dibromobenzhydrol. This is explained by assuming that in acetyl chloride solution two forms of the tetrabromobenzopinacone are present in mutual equilibrium. The difference between the forms lies in the distribution of affinity between the atoms of the molecule. Which of the two changes, intramolecular transformation or decomposition, a particular molecule undergoes is determined by the relative intensities of its main and subsidiary valencies. According to this theory, in the pinacone–pinacolin transformation, the elimination of water and the migration of the bromophenyl group take place simultaneously.

W. E. E.

2-Hydroxy-5-methoxy*cyclo*hexylcarbinol. L. HELFER (*Helv. Chim. Acta*, 1924, **7**, 950—956).—*p*-Hydroxyanisole is hydrogenated in the presence of reduced nickel to 4-*methoxy*cyclo*hexanol*, b. p. 204—205° (*acetyl* derivative, b. p. 102—103°/12 mm.). Oxidation by potassium dichromate and sulphuric acid leads to 4-*methoxy*-cyclo*hexanone* (b. p. 200—201°/760 mm., 72°/9 mm.; semicarbazone, m. p. 178°), which gives, with sodium ethoxide and *iso*amyl formate, 4-*methoxy*-2-*hydroxymethylene*cyclo*hexanone* (b. p. 108—110°/10 mm.). Sodium and alcohol reduce this to 6-*hydroxy*-3-*methoxy*cyclo*hexylcarbinol*, b. p. 172—174°/13 mm. 2-Hydroxymethylene-4-methyl*cyclo*hexanone gives with semicarbazide a cyclic semicarbazone,  $\begin{array}{l}CH_2—CH_2—C{=}N\\ |\qquad\qquad\quad\ |\\ CHMe·CH_2·C{:}CH\end{array}\!\!>N·CO·NH_2$, m. p. 161°. It is reduced in the same way as the corresponding methoxy compound (above) to 2-*hydroxy*-5-*methyl*cyclo*hexylcarbinol*, m. p. 70°. The action of formaldehyde on *p*-hydroxyanisole in the presence of calcium hydroxide gives 2-*hydroxy*-5-*methoxybenzyl alcohol* (m. p. 81°) and a little 2-*hydroxy*-5-*methoxy*-m-*xylylene glycol*, m. p. 127°.

W. E. E.

Effect of Sulphur on the Colour of certain Phthaleins. H. S. HOLT and E. E. REID (*J. Amer. Chem. Soc.*, 1924, **46**, 2333—2337).—By condensing *p*-hydroxybenzoyl-*o*-benzoic acid with *o*-hydroxyphenyl thio-ethers in the presence of zinc chloride (cf. Orndorff and Murray, A., 1917, i, 339), a series of derivatives of phenolphthalein containing the alkylthiol (or alkylsulphone) group ortho to hydroxyl has been obtained. The products form oximes, acetates, and benzoates, but the acetates could not be crystallised or the benzoates purified. The introduction of the methylthiol group changes the colour of the phenolphthalein in alkaline solution to purple, but the auxochrome effect diminishes with increasing weight of the alkyl group. The phenylthiol group has practically no effect and the methylsulphone group none. The p_H value of the indicator is only slightly affected. Similar products were obtained by condensing *p*-hydroxybenzoyl-*o*-benzoic acid with phenyl mercaptan, *o*-nitrophenyl mercaptan, *p*-nitrophenyl methyl sulphide, and *o*-nitrophenyl methyl sulphide, but were not purified.



The following thio-ethers were obtained by diazotisation of the corresponding *o*-amino derivative: o-*hydroxyphenyl methyl sulphide*, b. p. 105°/22 mm., d_{25}^{25} 1·168; o-*hydroxyphenyl amyl sulphide*, b. p. 125°/10 mm., d_{25}^{25} 1·061; *phenyl* o-*hydroxyphenyl sulphide*, m. p. 44°, and o-*hydroxyphenylmethylsulphone*, m. p. above 220°. The following ethers of 3-*thiolphenolphthalein* (annexed formula) have been obtained: *methyl*, p_H 8·4—10, *oxime*, m. p. 189° (decomp.); *amyl*, p_H 8·6—9·8, *oxime*, m. p. 175—176° (decomp.); *phenyl*, p_H 9·0—10, *oxime*, m. p. 190° (decomp.). 4 : 4′-*Dihydroxydiphenylphthalide*-3-*methylsulphone* has p_H 9·6, *oxime*, m. p. 165—167° (decomp.). Fusion of phthalic anhydride (1 mol.) with *o*-hydroxyphenyl methyl sulphide (2 mols.) and zinc chloride at 180° yields a salmon-coloured *hydroxymethylthiolanthraquinone*, m. p. 188° (decomp.).

R. B.

Diacylamides. I. K. Brunner, W. Seeger, and S. Dittrich (*Monatsh.*, 1924, **45**, 69—86; cf. Brunner, A., 1915, i, 1007; Miller, A., 1916, i, 203; Wolchowe, A., 1916, i, 844).—Diacylamides react with secondary hydrazines and aromatic amines to give substituted hydrazidines and amidines, respectively, in addition to acetylated derivatives, thus resembling nitriles. Diacetamide and *as*-phenylmethylhydrazine (equivalent quantities) were digested in 10% acetic acid at 100° for 24 hours; the fraction, b. p. 160—185°/13—17 mm., was freed from much acetylated hydrazine by crystallisation and the residue converted by ethereal oxalic acid into the *oxalate* of acetophenylmethylhydrazidine, m. p. 129—130°. Treatment with barium hydroxide gave the *base*,

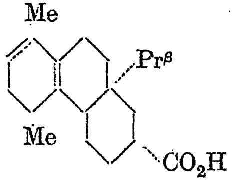
NMePh·NH·CMe:NH,

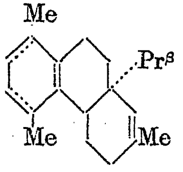
m. p. 83—84° (yield 7%); *picrate*, m. p. 158—159°; *dibenzoyl* derivative, m. p. 148—149°; *methiodide*, m. p. 210° (decomp.).

Dibenzamide and aniline do not condense in presence of sodium (cf. Walther, A., 1894, i, 503; Lottermoser, A., 1897, i, 38), but by heating equivalent amounts of the amide and aniline hydrochloride at 140—145° benzphenylamidine, m. p. 113·5°, is formed in 10% yield, together with benzanilide and benzamide from a by-reaction, and benzoic acid. The hydrochloride, m. p. 224°, and chloroplatinate are described. The reaction does not depend on the formation of benzonitrile, which does not react with aniline hydrochloride at so low a temperature. Dibenzamide does not react similarly with dimethylaniline hydrochloride, but with diphenylaniline hydrochloride at 170° it gives benzdiphenylamidine, CPh(:NH)·NPh_2, m. p. 112°. F. M. H.

Higher Terpene Compounds. XXIII. *d*-Pimaric Acid. L. Ruzicka and F. Balas (*Helv. Chim. Acta*, 1924, 7, 875—885; cf. A., 1923, i, 818).—When *d*-pimaric acid is dehydrogenated by means of sulphur, it gives a dimethylphenanthrene, $C_{16}H_{14}$; it loses not only a carboxyl group, but also three other carbon atoms, which are taken to represent a tertiary *iso*propyl group. Together with the evidence of molecular refraction, this result leads to the conclusion that *d*-pimaric acid is probably a dimethyl*iso*propyldecahydrophenanthrenecarboxylic acid. When dehydrogenated by means of sulphur, ethyl *d*-pimarate gives the same product as the acid itself. In order to locate the carboxyl group, ethyl *d*-pimarate is reduced to d-*pimarol*, $C_{20}H_{32}O$, b. p. 166—168°/0·1 mm., d_4^{15} 1·0114, n_D^{15} 1·5357, from which, by elimination of water, *methyl*-d-*pimarin*, $C_{20}H_{30}$, b. p. 140—145°/0·3 mm., d_4^{23} 0·9587, n_D^{23} 1·5301, is obtained. Dehydrogenation of this compound by means of sulphur gives a new *trimethylphenanthrene*, $C_{17}H_{16}$, m. p. 81° (*picrate*, m. p. 115°; *quinone*, m. p. 154°; *quinoxaline*, m. p. 154°), in which the methyl group derived from the carboxyl group of *d*-pimaric acid is still present. Hence this methyl group, and therefore the original carboxyl group, cannot be tertiary. This result is also to be expected from the difficulty with which *d*-pimaric acid is esterified. The trimethylphenanthrene from methyl-*d*-pimarin oxidises to a quinone of the same number of carbon atoms, therefore in *d*-pimaric acid positions 9 and 10 of the phenanthrene nucleus are vacant. The subjoined formula I is accordingly proposed for *d*-pimaric acid.

(I.)





(II.)

When *d*-pimaric acid is converted into methyl-*d*-pimarin, a third double bond, adjacent to the carboxyl group, is produced. But methyl-*d*-pimarin is highly unsaturated, and it follows that the two double bonds of *d*-pimaric acid cannot be in the same ring as the carboxyl group. On the other hand, dehydrogenation with nickel and palladium introduces only one more double bond into methyl-*d*-pimarin, forming *dehydromethyl*-d-*pimarin*, $C_{20}H_{28}$, b. p. 185—195°/12 mm., d_4^{14} 0·9771, n_D^{14} 1·5404 (formula II). This is explained if the double bonds of *d*-pimaric acid are as shown in I; the tertiary *iso*propyl group common to the two rings prevents their dehydrogenation. That there is probably no double bond adjacent to the carboxyl group of *d*-pimaric acid follows from the fact that the Bouveault reduction of simple αβ-unsaturated esters always leads to a saturated product. When *d*-pimaryl chloride is distilled in a vacuum, d-*pimarin*, $C_{19}H_{28}$, b. p. 182—184°/12 mm., $[\alpha]_D$ +109°, d_4^{15} 0·9693, n_D^{15} 1·5349, is obtained. This compound contains

three double bonds, and the fact that it is unsaturated supports the former conclusion that the two double bonds of *d*-pimaric acid are not in the same ring as the carboxyl group. The partial dehydrogenation of *d*-pimarin gives *dehydro*-d-*pimarin*, $C_{19}H_{26}$, b. p. 203—212°/12 mm., d_4^{15} 0·9863, n_D^{15} 1·5505, which is notably less unsaturated than *d*-pimarin. This is further support for the structure of *d*-pimaric acid given, since dehydro-*d*-pimarin, like its higher homologue, II, contains a benzene nucleus. d-*Pimarin*, obtained by heating *d*-pimaric acid at 310°, has b. p. 184—186°/12 mm., $[\alpha]_D$ +30·1° in 4% chloroform solution, d_4^{23} 0·9717, n_D^{23} 1·5406.
W. E. E.

Derivatives of Hexamethylenetetramine. GEHE u. Co. A.-G., and H. RUNNE (D.R.-P. 386691; from *Chem. Zentr.*, 1924, i, 2612).—By combining aryloxyacetic acids with hexamethylenetetramine, the bitter taste of the acids is neutralised, the salts having a slightly sweet after-taste; they are useful as internal or external antiseptics. The following salts, prepared in the usual way, are described: *phenoxyacetate*, sinters about 177°; p-*tolyloxyacetate*, sintering about 194°; *guaiacolglycollate*, sintering about 130°; *salicyloxyacetate* (1 mol. acid +2 mols. base), sintering about 86°; *acid salicyloxyacetate* (1 mol. acid +1 mol. base) crystallises slowly and is more hygroscopic than the neutral salt. F. A. M.

Halogenated Anhydrides of o-Hydrocoumaric Acid [Melilotic Acid]. CHEMISCHE WERKE GRENZACH A.-G. (D.R.-P. 386619; from *Chem. Zentr.*, 1924, i, 2633).—Halogenated coumarins or halogenated *o*-coumaric acids are treated with reducing agents and the resulting halogenated *o*-hydrocoumaric acids converted into the anhydrides by heating. 3 : 5-*Dichlorocoumarin*, m. p. 157° (from 3 : 5-dichlorosalicylaldehyde) on reduction with sodium amalgam in aqueous suspension yields 3 : 5-*dichloromelilotic acid*, m. p. 122°, which on heating at 210° gives the *anhydride*, m. p. 107°, b. p. 204°/25 mm. 5-*Chlorocoumarin* (from 5-chlorosalicylaldehyde), m. p. 165°, is reduced by sodium amalgam to 5-chloromelilotic acid, m. p. 142°, giving the anhydride, m. p. 109°, b. p. 192°/20 mm. The anhydrides are of value against intestinal parasites. F. A. M.

Elemic Acid from Manila Elemi Resin. H. LIEB and D. SCHWARZL (*Monatsh.*, 1924, **45**, 51—61).—To α-elemic acid from *Canarium commune* is assigned the formula $C_{27}H_{42}O_3$ (contrast Tschirch and Cremer, A., 1902, i, 812; Buri, A., 1878, ii, 439); it is transformed by light into a resin which is regarded as identical with Tschirch and Cremer's β-acid.

α-Elemic acid, m. p. 215°, is a monocarboxylic acid; $[\alpha]_D^{19}$ −24·48° in alcohol. There are described: *potassium* salt (+$5H_2O$), becoming anhydrous at 115°, hydrolysed by water; *sodium* salt (+$5H_2O$); amorphous *silver* salt, which with methyl iodide gives the *monomethyl* ester (gummy). Tschirch and Cremer's preparation of an acetyl and benzoyl derivative could not be repeated.

Oxidation of α-elemic acid with chromic oxide in acetic acid gave a monocarboxylic *acid*, $C_{27}H_{40}O_3$, m. p. 274°, $[\alpha]_D^{18}$ −67·13°

in chloroform; *sodium* salt ($+7H_2O$). Although attempts to prepare a crystalline oxime, semicarbazone, or hydrazone were unsuccessful, it is regarded as a ketonic acid, and the name "elemonic acid" is suggested for it; α-elemic acid must then contain a secondary alcoholic group, and for it is suggested the name "elemolic acid." Both readily take up bromine, whilst subsequent elimination of hydrogen bromide leaves an amorphous residue.

Oxidation of α-elemic acid with nitric acid gave an amorphous acid, $C_{21}H_{25}O_{10}N_3$ (cf. Tschirch and Cremer, *loc. cit.*), decomp. 175°; *silver* salt, $C_{21}H_{23}O_{10}N_3Ag_2$. [Cf. *B.*, 1924, 952.]

F. M. H.

Ring-chain Tautomerism. X. Inhibited Tautomerism. F. Dickens, L. Horton, and J. F. Thorpe (*J. Chem. Soc.*, 1924, **125**, 1830—1840).—From *cyclo*hexanone cyanohydrin (Higson and Thorpe, T., 1906, **89**, 1455) and ethyl sodiocyanoacetate, *ethyl* 1-*cyano*cyclo*hexane*-1-*cyanoacetate*, m. p. 54°, b. p. 210—212°/22 mm., is obtained. When hydrolysed, it affords 1-carboxy*cyclo*hexane-1-acetic acid. The sodium derivative of the ester decomposes when its solution is evaporated, yielding 1-*cyano*cyclo*hexane*-1-*acetonitrile*, m. p. 84°, and *sodium* 1-*cyano*cyclo*hexane*-1-*cyanoacetate*, m. p. 145—149° (*silver* and *aniline* salt [m. p. 98°] also described). When a solution of this sodium salt (which is the main product when a small excess of sodium is used in the hydrolysis) is acidified and the oily precipitate first formed redissolved in an excess of hydrochloric acid, 1-*carbamyl*cyclo*hexane*-1-*cyanoacetic acid*, m. p. 90° (decomp. 100°), crystallises (*sodium* salt, m. p. 105—108°). When heated at 72—74° this acid affords ammonium 1-carboxy*cyclo*hexane-1-acetate, together with the *imide* of α-*carbamyl*-1-*carboxy*cyclo*hexane*-1-*acetic acid*, m. p. 152° (decomp.); when it is treated with acetic acid, the *imide* of 1-*carboxy*cyclo*hexane*-1-*cyanoacetic acid*, m. p. 123—124°, is obtained, and this, when boiled with aqueous potassium hydroxide, affords α-*carbamyl*-1-*carboxy*cyclo*hexane*-1-*acetic acid*, m. p. 126°, which is converted at its melting point into the *imide* of 1-*carboxy*cyclo*hexane*-1-*acetic acid*, m. p. 145° (this is also obtained by interaction of 1-carboxy*cyclo*hexane-1-acetic anhydride and carbamide). When 1-cyano*cyclo*hexane-1-acetonitrile is dissolved in concentrated sulphuric acid, it is converted into 1-*carbamyl*cyclo*hexane*-1-*acetamide*, m. p. 201°.

When the sodium compound of ethyl αβ-dicyano-ββ-dimethylpropionate (Higson and Thorpe, *loc. cit.*) is treated with water it affords a mixture of (i) *as*-dimethylsuccinonitrile, m. p. 68° (this is best prepared by boiling the solution and is not a liquid as stated by Hell and Rothberg [A., 1889, 959]); (ii) the *imide* of α-*cyano*-ββ-*dimethylsuccinic acid*, m. p. 116°, and (iii) β-*carbamyl*-α-*cyano*-ββ-*dimethylpropionic acid*, m. p. 142°. The first is converted by cold concentrated sulphuric acid into as-*dimethylsuccinamide*, m. p. 153°, and (iii) is converted into (ii) by hot acetic acid.

*cyclo*Heptanone cyanohydrin condenses with ethyl sodiocyanoacetate to give *ethyl* 1-*cyano*cyclo*heptane*-1-*cyanoacetate*, b. p.

201°/13 mm., the sodium compound of which, when treated with water and the solution evaporated to dryness, yields the corresponding sodium salt. The free acid cannot be obtained; a solution of the sodium salt yields when acidified solely the *imide* of 1-*carboxy*cyclo*heptane*-1-*cyanoacetic acid*, m. p. 130°. The sodium salt is accompanied by some 1-*cyano*cyclo*heptane*-1-*acetonitrile*, m. p. 58°. When ethyl 1-cyano*cyclo*heptane-1-cyanoacetate is dissolved in concentrated sulphuric acid and the diluted solution boiled, the *imide* of 1-*carboxy*cyclo*heptane*-1-*acetic acid*, m. p. 116°, is formed, together with a little 1-*carboxy*cyclo*heptane*-1-*acetic acid*, m. p. 153°.

The parent compounds of all three series are ββ-disubstituted αβ-dicyanopropionic acids; the mechanism of the various reactions is discussed on the lines indicated by the title of the paper, the effect of the different modes of ββ-substitution on the proximity of the other groups being kept in view. W. A. S.

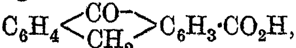
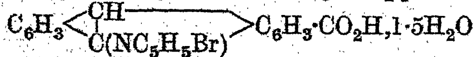
Isomeric Esters of *p*-Ethoxybenzoylacrylic Acid. G. P. Rice (*J. Amer. Chem. Soc.*, 1924, **46**, 2319—2326).—In view of the difference between the isomeric esters of benzoylacrylic acid (A., 1923, i, 218) and of *p*-methoxybenzoylacrylic acid (this vol., i, 287), the isomeric methyl and ethyl esters of *p*-ethoxybenzoylacrylic acid have been investigated. The stable yellow esters, like those of *p*-methoxybenzoylacrylic acid, are isomerised on exposure to sunlight in benzene solution, and the reverse change is effected in benzene solution containing a crystal of iodine. The methyl ester of the ethoxy compound, unlike that of the methoxy compound, is not polymerised on exposure to sunlight in the solid state, isomerisation alone taking place, and since the methoxy ester has the higher m. p., the physical state of the substance does not appear to be the sole determinant of polymerisation or isomerisation. *p*-Ethoxybenzoylacrylic acid itself does not polymerise on exposure to light. Both yellow and colourless esters are partly hydrolysed by dilute sodium carbonate and cold concentrated hydrochloric acid, yielding *p*-ethoxybenzoylacrylic acid, boiling dilute hydrochloric acid yielding also α-hydroxy-β-*p*-ethoxybenzoylpropionic acid. The colourless esters are first transformed into the yellow esters by hydrochloric acid. With semicarbazide, the esters of the *p*-ethoxy-acid behave like those of the *p*-methoxy-acid. The colourless esters yield an additive compound and its semicarbazone; the yellow esters yield, in addition, two isomeric semicarbazones. This reaction establishes the isomerism of the colourless ethyl ester, which could only be obtained liquid. *p*-Ethoxybenzoylacrylic acid itself yields a semicarbazone.

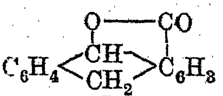
Methyl p-*ethoxybenzoylpropionate*, m. p. 53°, is converted by Kohler and Engelbrecht's method (A., 1919, i, 330) into *methyl* p-*ethoxybenzoylacrylate*, yellow needles, m. p. 81·5°; the colourless *isomeride*, m. p. 53°, can be obtained by direct esterification of p-*ethoxybenzoylacrylic acid*, yellow needles, m. p. 141—142° (*semicarbazone*, $C_{13}H_{15}O_4N_3$, m. p. 212° [decomp.]), obtained in 62% yield from maleic anhydride and phenetole by the Friedel–Crafts reaction. *Ethyl* p-*ethoxybenzoylpropionate*, m. p. 51°, similarly yields *ethyl* p-*ethoxybenzoylacrylate*, yellow needles, m. p. 54°; colourless *isomeride*, an oil. On bromination in chloroform, methyl *p*-ethoxybenzoylacrylate yields a *dibromo* compound, $C_{13}H_{14}O_4Br_2$, m. p. 92°, the ethyl ester similarly yielding the *dibromo* derivative, $C_{14}H_{16}O_4Br_2$, m. p. 81°. Bromination of *p*-ethoxybenzoylacrylic acid in acetic acid yields *αβ-dibromo*-β-p-*ethoxybenzoylpropionic acid*, m. p. 151°. Hydrolysis of the esters of *p*-ethoxybenzoylacrylic acid with hydrochloric acid yields *α-hydroxy*-β-p-*ethoxybenzoylpropionic acid*, m. p. 132°. Colourless methyl *p*-ethoxybenzoylacrylate with 2 mols. of semicarbazide hydrochloride in methyl alcohol in the presence of sodium acetate yields *methyl α-semicarbazido*-β-p-*ethoxybenzoylpropionate*, m. p. 169°, together with the *semicarbazone* of the semicarbazide, m. p. 176° (decomp.). The yellow ester, on similar treatment, yields in addition to these two substances, the two isomeric *methyl* p-*ethoxybenzoylacrylate semicarbazones*, yellow, m. p. 173°, colourless, m. p. 149°. Similarly, colourless ethyl *p*-ethoxybenzoylacrylate yields *ethyl α-semicarbazido*-β-p-*ethoxybenzoylpropionate*, m. p. 154°, and its *semicarbazone*, m. p. 183° (decomp.), whilst the yellow isomeride yields in addition the two isomeric *ethyl* p-*ethoxybenzoylacrylate semicarbazones*, plates, m. p. 155°, and yellow needles, m. p. 140°.

R. B.

Terephthalic Acid Derivatives. M. T. BOGERT and P. S. NISSON (*Proc. Nat. Acad. Sci.*, 1924, **10**, 426—433; cf. A., 1920, i, 65).—*p*-Dihydroxy*iso*propylbenzene (*loc. cit.*) shows little or no physiological activity and has none of the properties of a local anæsthetic. Methyl terephthalate and magnesium ethyl iodide yield, not the expected pinacone, but p-*di*(*α-ethylpropenyl*)*benzene*, b. p. 149—151°/20 mm., in 46% yield. When magnesium *n*-butyl bromide is used, a gum, containing some unsaturated hydrocarbon, is obtained. Magnesium aryl halides, but not the alkyl derivatives, interact with terephthaloyl chloride to produce compounds of the type $COR{\cdot}C_6H_4{\cdot}COR$; thus, magnesium phenyl bromide affords *p*-dibenzoylbenzene. Methyl aminoterephthalate (cf. Kaufmann and Weissel, A., 1912, i, 863) interacts with ethyl iodide at 100° to give *methyl ethylaminoterephthalate*, m. p. 83·5°, and with ethyl sulphate at 150° to give *methyl diethylaminoterephthalate*, b. p. 191—192°/20 mm. When methyl aminoterephthalate is treated with magnesium methyl or ethyl bromide, or magnesium *n*-butyl bromide, only gummy products are obtained. Methyl dimethylaminoterephthalate (Kaufmann and Weissel, *loc. cit.*) and magnesium methyl iodide afford no pinacone, but 2 : 5-*di*iso*propenyldimethylaniline*, m. p. 62—63°; 2 : 5-*di*iso*propenyldiethylaniline* (?), b. p. 195—197°/18 mm., was similarly obtained. Methyl aminoterephthalate yields, however, with magnesium phenyl bromide, a glycol (pinacone), viz., 2 : 5-*di*(*hydroxydiphenylmethyl*)*aniline*, m. p. 202°; the dimethylamino and diethylamino esters similarly afforded 2 : 5-*di*(*hydroxydiphenylmethyl*)*dimethylaniline*, m. p. 185°, and 2 : 5-*di*(*hydroxydiphenylmethyl*)*diethylaniline*, m. p. 179°, respectively. These compounds are sparingly soluble and valueless pharmacologically. W. A. S.

Synthesis of 3 : 5-Dihydroxycinnamic Acid. Y. Asahina and T. Matsuzaki (*J. Pharm. Soc. Japan*, 1924, No. 509, 527—539).—3 : 5-Dihydroxybenzoic acid is prepared by heating a mixture of 100 g. of benzoic acid, 100 g. of phosphoric oxide, and 300 g. of fuming sulphuric acid (50% SO_3) at 280—300° for 10 hours, followed by fusion with potassium hydroxide (cf. Barth and Senhofer, *Annalen*, 1871, **159**, 217). The acid is changed into 3 : 5-dimethoxybenzaldehyde, through $(OMe)_2C_6H_3{\cdot}CO{\cdot}NHPh$, $(OMe)_2C_6H_3{\cdot}CCl{:}NPh$, and $(OMe)_2C_6H_3{\cdot}CH{:}NPh$. By applying Perkin's reaction to the aldehyde, 3 : 5-dimethoxycinnamic acid, m. p. 174°, is produced. On heating with hydrogen iodide, bromide, or other reagents, it gives no dihydroxy compound. When $(OMe)_2C_6H_3{\cdot}CCl{:}NPh$ is treated with zinc chloride, hydrogen chloride, and ether, a *chloro*-3 : 5-*dimethoxybenzaldehyde*, m. p. 129°, is obtained; *oxime*, m. p. 125°. When Perkin's reaction is applied to crude 3 : 5-diacetoxybenzaldehyde and the resulting acid is hydrolysed with sodium carbonate, 3 : 5-dihydroxycinnamic acid, $C_9H_8O_4,0{\cdot}5H_2O$, m. p. 244—245° (decomp.), is formed. It gives the above dimethyl derivative, m. p. 174°, by treatment with methyl sulphate. K. K.

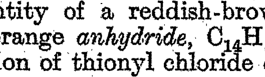
Anthraquinonecarboxylic Acids. E. de B. Barnett, J. W. Cook, and H. H. Grainger (*Ber.*, 1924, **57**, [*B*], 1775—1781).—Anthraquinone-1-carboxylic acid is reduced by zinc and fuming hydrochloric acid in the presence of glacial acetic acid to a mixture of 10-anthrone-1-carboxylic acid,  $C_6H_4{<}{}^{CO}_{CH_2}{>}C_6H_3{\cdot}CO_2H$, m. p. 252°, and the *lactone* of 9 : 10-dihydro-9-anthranol-1-carboxylic acid (I), m. p. 277—278° after darkening at 264°; the latter compound is converted by boiling alcoholic potassium hydroxide solution into anthracene-1-carboxylic acid. The action of nitric acid (*d* 1·5) and glacial acetic acid on anthracene-1-carboxylic acid yields primarily the *acetate* of a nitrodihydroanthranol-1-carboxylic acid, m. p. 172° (decomp.), which is converted by pyridine into 9(? 10)-*nitroanthracene*-1-*carboxylic acid*, decomp. 249°. Anthracene-1-carboxylic acid is readily brominated in boiling glacial acetic acid to 9(? 10)-*bromoanthracene*-1-*carboxylic acid*, m. p. 281—282° (decomp.), but bromination does not proceed beyond this stage when excess of halogen is used. The action of bromine on anthracene-1-carboxylic acid in the presence of pyridine yields *anthracyl*-10-*pyridinium bromide*-1-*carboxylate*,  $C_6H_3{<}{}^{CH}_{C(NC_5H_5Br)}{>}C_6H_3{\cdot}CO_2H,1{\cdot}5H_2O$. *Phenyl anthracene*-1-*carboxylate*, m. p. 207—209°, is converted by bromine (2 g.-mol.) into the ester of the monobromo-acid, but by a large excess of bromine into a mixture of the esters of the mono- and dibromo-acids. Anthracene-2-carboxylic acid, conveniently obtained



(I.)

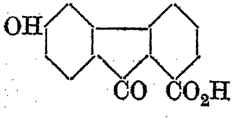
by the reduction of 9-anthrone-2-carboxylic acid with zinc dust and ammonia, resembles the isomeric acid in its behaviour during nitration, yielding initially an additive product which is transformed by pyridine into a mixture of isomeric nitroanthracene-carboxylic acids which has not been separated into its components. On the other hand, it is transformed by bromine into a *dibromoanthracene-2-carboxylic acid*, m. p. 335° (decomp.). 9-Anthrone-2-carboxylic acid is converted by acetic anhydride and pyridine into its *acetyl* derivative, m. p. 253—255° (decomp.), which is transformed by nitration and subsequent acetylation of the product into 10-*nitro-9-acetoxyanthracene-2-carboxylic acid*, m. p. 228° (decomp.), after previous softening. H. W.

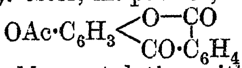
2 : 4-Dihydroxybenzoyl-*o*-benzoic Acid and some of its Derivatives. W. R. Orndorff and E. Kline [with C. V. Shapiro] (*J. Amer. Chem. Soc.*, 1924, **46**, 2276—2291).—2 : 4-Dihydroxybenzoyl-*o*-benzoic acid, m. p. 208—209° (decomp.), is obtained in 68% yield by heating phthalic anhydride with resorcinol at 126°, the use of boric acid (Fischer and Bollmann, A., 1922, i, 936) being unnecessary. The acid is also obtained (in 89·5% yield) by decomposition of fluorescein with sodium hydroxide, whilst on heating above its melting point the acid is converted into fluorescein, phthalic anhydride, and water. The γ-fluorescein described by Liebig (A., 1912, i, 376) was not obtained, but the reactions prove that the formation of fluorescein takes place in two stages, the intermediate product being 2 : 4-dihydroxybenzoyl-*o*-benzoic acid, which is colourless when pure, and melts to a red liquid. Contrary to Baeyer's statement, well-crystallised *ammonium, sodium, potassium, silver, barium, calcium, zinc* (m. p. 80—90°), and *lead* salts have been prepared, to which the ketonic structure, $(OH)_2C_6H_3\cdot CO\cdot C_6H_4\cdot CO_2M$, is assigned, the lactone structure,



$$\begin{array}{l}(OH)_2C_6H_3\cdot\underset{|}{C}(OH)\cdot\underset{|}{C}_6H_4\\ \qquad\qquad\quad O\text{————}CO\end{array}$$

being attributed to the free acid (cf. Orndorff and Kelley, A., 1922, i, 833). On heating with acetic anhydride and sodium acetate, the acid is converted into a colourless *triacetate*, $C_{14}H_7O_5Ac_3$, m. p. 134—135°, and not a diacetate as stated by Liebig (*loc. cit.*), which is readily hydrolysed by alcoholic sodium hydroxide, yielding the dihydroxy-acid and a small quantity of a reddish-brown substance probably identical with the orange *anhydride*, $C_{14}H_8O_4$, m. p. above 350°, obtained by the action of thionyl chloride on either the crude yellow or the pure dihydroxy-acid. The orange anhydride gives a deep red solution in sodium hydroxide which does not yield the dihydroxy-acid on boiling. The anhydride appears to give an acetate with acetic anhydride. The annexed formula is suggested for this anhydride. By treatment with excess of acetic anhydride the dihydroxy-acid yields the *anhydride* of the monoacetate described by Fischer and Bollmann (*loc. cit.*), $C_{14}H_7O_4Ac$, m. p. 135—136° (from glacial acetic acid), which when crystallised from dilute acetic acid yields Fischer and Bollmann's



monoacetate, m. p. 161—162°. Dilute ethyl and methyl alcohol similarly convert the anhydride into the *ethyl* ester, m. p. 62—66°, and *methyl* ester, m. p. 110°, respectively. This anhydride has the structure  $\mathrm{OAc{\cdot}C_6H_3}<\begin{array}{l}\mathrm{O{-}CO}\\ \quad\;\; | \\ \mathrm{CO{\cdot}C_6H_4}\end{array}$. The monoacetate itself could not be obtained by acetylation with acetic anhydride, whilst with acetyl chloride the crude yellow dihydroxy-acid yields the *diacetate* of 2 : 4-dihydroxybenzoyl-*o*-benzoic anhydride, m. p. above 350°, together with a small quantity of an isomeric substance, $(C_{14}H_8O_2)_2Ac_2O$, which does not melt below 300°. The diacetate dissolves in sodium hydroxide, giving a deep purple solution, from which, on boiling, the orange anhydride, $C_{14}H_8O_4$, described above, together with a little dihydroxy-acid, is precipitated, and not the anhydride, $(C_{14}H_9O_4)_2O$, as stated by Graebe. The pure dihydroxy-acid on similar treatment yields a colourless *substance*, $(C_{14}H_7O_4Ac)_2$, m. p. 291—293° (decomp.), practically insoluble in sodium hydroxide and yielding on boiling the dihydroxy-acid with only a small amount of the orange anhydride. Esterification of the dihydroxy-acid in the presence of sulphuric acid yields the *ethyl* ester, m. p. 133—134° (cf. Tambor, A., 1910, i, 558), and *methyl* ester, m. p. 191—192°. 2 : 4-Dihydroxybenzoyl-*o*-benzoic acid yields a *phenylhydrazone*, $C_{20}H_{14}O_3N_2$ (+EtOH, lost at 130°), m. p. 260—261°, whilst on bromination in glacial acetic acid 3 : 5-dibromo-2 : 4-dihydroxybenzoyl-*o*-benzoic acid, m. p. 224° (decomp.; cf. Heller, A., 1895, i, 235; Meyer, A., 1897, i, 69), is obtained, which on heating above its m. p. is converted into eosin and phthalic anhydride, and on heating with resorcinol and zinc chloride at 160—180° yields *as*-dibromofluorescein. Dry ammonia converts the dibromo-acid into the unstable *triammonium* salt, $C_{14}H_8Br_2O_5 + 3{\cdot}5NH_3$, which loses 2 mols. of ammonia in a vacuum and the remaining 1·5 mols. in a current of air at 85°. The dibromo-acid forms a *triacetate*, $C_{14}H_5Br_2O_5Ac_3$, m. p. 179—182°, and the *anhydride* of a monoacetate, $C_{14}H_5Br_2O_4Ac$, m. p. 200—201° (decomp.). On heating with acetyl chloride, the dibromo-acid yields 3 : 5-*dibromo*-2 : 4-*diacetoxybenzoyl*-o-*benzoic anhydride*, m. p. 218°. R. B.

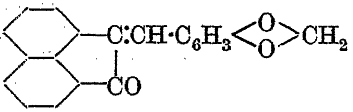
Bile Acids. XI. M. Schenck (*Z. physiol. Chem.*, 1924, **139**, 39—51).—The triketotricarboxylic acid, $C_{24}H_{32}O_9$, obtained by oxidation of *iso*bilianic acid (this vol., i, 179) is termed *bilisoidanic acid*; it reacts with hydroxylamine to form an amorphous monoxime. On reduction with zinc and acetic acid, dichloromonodeoxybilianic acid (Pregl, A., 1903, i, 318) gives a small yield of deoxybilianic acid; this establishes the position of the chlorine atoms in the former substance. E. S.

Compounds of Piperonal and Acetic Anhydride. W. P. Jorissen and P. A. A. van der Beek (*Rec. trav. chim.*, 1924, **43**, 586—590).—The fusion curve of piperonal and acetic anhydride up to 60 mol.% of the latter shows no sign of a compound. When the compounds are heated together at 100° for 24 hours in presence of a trace of hydrobromic acid or phosphorus trichloride (cf.

Blanksma, A., 1910, i, 680) a fusion curve is obtained which shows that, besides a 1 : 1 molecular compound, there also exists a labile compound of 2 mols. of piperonal and 1 mol. of acetic anhydride.

W. E. E.

Reaction of Aldehydes. III. R. DE FAZI (*Gazzetta*, 1924, **54**, 658—667; cf. A., 1921, i, 568).—With piperonal, cuminaldehyde, *m*-tolualdehyde, cinnamaldehyde, *p*-dimethylaminobenzaldehyde, and furfuraldehyde, fluorene yields unsaturated condensation products which give various colorations with concentrated sulphuric acid, but on reduction form compounds giving no such coloration. Acenaphthene does not yield condensation products with these cyclic aldehydes under the conditions employed by the author, but acenaphthenone reacts with such aldehydes in presence of sodium hydroxide, the resulting compounds giving violet-red colorations with concentrated sulphuric acid. These compounds cannot, however, be formed when acenaphthene and cyclic aldehydes are placed in contact with sulphuric acid, since such conditions lead neither to the formation of acenaphthenone nor, if the latter is added, to the formation of either condensation products or coloration. The results obtained with indones (A., 1921, ii, 357) show that, with some organic compounds containing closed nuclei, the same coloration with sulphuric acid may be determined by the presence of the cyclostatic group $-CO \cdot CH:CH-$ as by $-CH_2 \cdot CH:CH-$.



Piperonylideneacenaphthenone (annexed formula) forms canary-yellow needles, m. p. 159—160°; 4-*hydroxy*-3-*methoxybenzylideneacenaphthenone*, $C_{20}H_{14}O_3$, from acenaphthenone and vanillin, m. p. 149—150°; p-*methoxybenzylideneacenaphthenone*, $C_{20}H_{14}O_2$, from anisaldehyde, canary-yellow needles, m. p. 97—98°; *cinnamylideneacenaphthenone*, $C_{21}H_{14}O$, yellow needles, m. p. 167—168°; p-*dimethylaminobenzylideneacenaphthenone*, garnet-red, stellar aggregates of needles, m. p. 158—160°, and *furfurylideneacenaphthenone*, $C_{17}H_{10}O_2$, golden-yellow prisms, m. p. 142—143°.

T. H. P.

The Systems, Aldehydes–Organic Acids and Ketones–Organic Acids. M. PASSERINI (*Gazzetta*, 1924, **54**, 672—682).—The suggestion that, in the reaction of a carbylamine with an aldehyde or ketone in presence of an organic acid, the aldehyde or ketone first forms with the organic acid a labile additive compound (cf. A., 1922, i, 731) is verified by: (1) the electrical conductivities of mixtures of acetone with acetic acid, a minimum value being shown by the mixture containing the components in about molecular proportions; (2) the results of thermal analysis of the three systems formed by benzoic acid with *m*-nitrobenzaldehyde, piperonal, and benzil, respectively. These conclusions are in accord with those of Kendall and Brakeley (A., 1922, ii, 126). T. H. P.

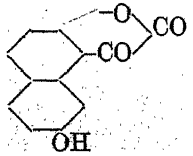
Carbylamines. XI. Reaction of Phenylcarbylamine with Anil Derivatives of Aromatic *o*-Hydroxyaldehydes. M. PASSERINI (*Gazzetta*, 1924, **54**, 667—671).—In the formation of dianil derivatives by the interaction of aromatic hydroxy compounds with carbylamines (cf. this vol., i, 57, 751 and succeeding abstract), either the carbylamine may act in its dimeric form, $(NR{:}C)_2$, or there may be two distinct stages, the anil derivative of the hydroxyaldehyde being formed first. The former of these interpretations is excluded by the observation that benzeneazophenylcarbylamine, which reacts in the same way as phenylcarbylamine with β-naphthol, has the simple molecular weight in freezing benzene. That the second explanation is the true one is shown by the formation of the dianil derivative of 2-hydroxy-1-naphthylglyoxal from phenylcarbylamine and the anil derivative of 2-hydroxy-1-naphthaldehyde, and by that of the dianil derivative of *o*-hydroxyphenylglyoxal from salicylideneaniline and phenylcarbylamine; benzylideneaniline does not, however, react with phenylcarbylamine under the conditions used.

The reaction between phenylcarbylamine and naphthols or phenol is evidently determined by the presence of the hydroxyl group, which imparts special properties to the methinic group in the ortho position; the same influence is probably exerted by the hydroxyl group of the anil derivatives of the hydroxyaldehydes.

T. H. P.

Carbylamines. X. Reaction of Aromatic Carbylamines with Naphthols and with Phenols. M. Passerini (*Gazzetta*, 1924, **54**, 633—640).—The action of phenylcarbylamine on various hydroxy derivatives of benzene and naphthalene has been investigated (cf. this vol., i, 57, 751). With 2 : 7-dihydroxynaphthalene, the reaction is similar to that occurring with β-naphthol, 2 mols. of the carbylamine and 1 mol. of the hydroxy compound interacting; no tetra-anil is obtained. Phenol, thymol, and resorcinol also react with phenylcarbylamine, but the products formed are syrupy, and only in the first case could a small amount of the dianil be separated. The reaction proceeds well with β-naphthol and benzeneazophenylcarbylamine.

The *dianil* derivative of 2 : 7-*dihydroxy*-1-*naphthylglyoxal*, $C_{10}H_5(OH)_2\cdot C({:}NPh)\cdot CH{:}NPh$, obtained from 2 : 7-dihydroxynaphthalene and phenylcarbylamine, forms pale yellow needles, m. p. 174—176°, and its *dibenzoyl* derivative, $C_{38}H_{26}O_4N_2$, orange-red crystals, m. p. 154—156° (decomp.). Phenylhydrazine converts the dianil into 2 : 7-*dihydroxy*-1-*naphthylglyoxal diphenylhydrazone*, $C_{10}H_5(OH)_2\cdot C({:}N\cdot NHPh)\cdot CH{:}N\cdot NHPh$, m. p. 220° (decomp.), and, when boiled with potassium hydroxide solution, the anil yields the *lactone* of 2 : 7-*dihydroxy*-1-*naphthylglyoxylic acid* (annexed formula), which has a distinctly acid reaction and forms lustrous, yellow crystals, decomp. 280—282°; 2 : 7-*dihydroxynaphthalene*-1-*carboxylic acid*, obtained by oxidising this lactone with hydrogen peroxide in acetic acid solution, has m. p. 275°.



The *dibenzeneazoanil* derivative of 2-*hydroxy*-1-*naphthylglyoxal*, $OH\cdot C_{10}H_6\cdot C({:}N\cdot C_6H_4\cdot N{:}NPh)\cdot CH{:}N\cdot C_6H_4\cdot N_2Ph$, forms minute, dark-red crystals, m. p. 263°, and is converted by phenylhydrazine into 2-hydroxy-1-naphthylglyoxal diphenylhydrazone (cf. this vol., i, 57).

The *dianil* derivative of o-*hydroxyphenylglyoxal*,

$$OH{\cdot}C_6H_4{\cdot}C(:NPh){\cdot}CH:NPh,$$

obtained from phenol and phenylcarbylamine, yellow needles, m. p. 150—152°, yields *o*-hydroxyphenylglyoxal diphenylhydrazone when treated with phenylhydrazine. T. H. P.

Catalytic Reduction of Oximes in the Presence of Colloidal Palladium. W. Gulewitsch.—(See i, 1285.)

Magnesium Acetylenyl Bromide. J. Salkind and A. Rosenfeld.—(See i, 1291.)

Electrolytic Reduction of Piperitone. A. R. Penfold and F. R. Morrison (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 215—217).—An almost quantitative yield of *iso*menthone is obtained by the electrolytic reduction of piperitone. [Cf. *B.*, 1924, 926.]

W. T. K. B.

Phenacyl Mercaptan and Related Substances. B. Groth (*Arkiv Kem., Min., Geol.*, 1924, **9**, No. 1, 1—63).—The preparation of phenacylmercaptan by several methods is described; a number of its derivatives and certain phenacylthiocarbonates were also prepared.

The interaction of phenacyl bromide and sodium hydrogen sulphide solution at 15° gives only 13% of the theoretical yield of phenacyl mercaptan, together with diphenacyl sulphide. Phenacyl bromide with Bender's salt in aqueous alcohol at 0° gives S-*phenacyl* O-*ethyl thiocarbonate*, $C_{11}H_{12}O_3S$, b. p. 152°/1·6 mm., 175—176°/3 mm., d_4^{15} 1·1948, n_D^{15} 1·554; *semicarbazone*, m. p. 142—143°; with potassium xanthate it gives S-*phenacyl* O-*ethyl dithiocarbonate*, m. p. 32° (*phenylhydrazone*, m. p. 64°); with potassium trithiocarbonate it gives *phenacyl trithiocarbonate*, $(COPh{\cdot}CH_2{\cdot}S)_2CS$ (yield 90%), obtained in two forms, m. p. 103—104° and m. p. 110°; *bisphenylhydrazone*, m. p. 139—140°, after keeping, m. p. 146—147°. Alkaline hydrolysis of these thiocarbonates, under varying conditions, gave no phenacyl mercaptan, showing the sulphur atom to be loosely attached to the phenacyl group. Boiling 20% nitric acid with the third ester gave benzoic acid and at 60—70° gave SS-*diphenacyl dithiocarbonate*, m. p. 98°; *bisphenylhydrazone*, m. p. 162° (decomp.).

Phenacyl bromide reacts with potassium carbothiolonglycollate solution at 0°, forming phenacyl trithiocarbonate and *phenacylcarbothiolonglycollic acid*, $COPh{\cdot}CH_2{\cdot}S{\cdot}CS{\cdot}O{\cdot}CH_2{\cdot}CO_2H$, m. p. 107°, which is precipitated by acidification of the filtrate; it forms acid *sodium* and *potassium* salts; *calcium* ($+4H_2O$), *strontium* ($+5H_2O$), *barium* ($+2H_2O$), *cupric*, *lead*, *magnesium*, and *zinc* salts; *methyl* ester, m. p. 76°; *ethyl* ester, m. p. 51°; *phenylhydrazone*, m. p. 119—120°. Hydrolysis with acetic acid gave a good yield of phenacyl mercaptan. Hydrolysis with sodium carbonate gave diphenacyl disulphide, and acetophenone or phenacyl trithiocarbonate according to the conditions; alcoholic potassium hydroxide gave potassium carbothiolonglycollate (cf. Ahlqvist, A., 1919, i, 435). Oxidation of phenacylcarbothiolonglycollic acid with neutral permanganate gives *phenacylcarbothiolglycollic acid*, $COPh·CH_2·S·CO_2·O·CH_2·CO_2H$, m. p. 77° (yield 80%); acid *sodium* salt; *barium* salt ($+3H_2O$); *phenylhydrazone*, m. p. 136—137°. By the action of water or weak acid, this also gave phenacyl mercaptan, yield 68%.

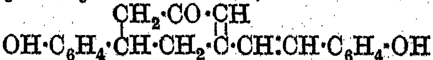
Potassium dithiocarbaminoacetate (cf. Körner, A., 1908, i, 509) with phenacyl bromide forms *phenacyldithiocarbaminoacetic acid*, $COPh·CH_2·S·CS·NH·CH_2·CO_2H$, m. p. 103° (yield 88%); *sodium* salt ($+2H_2O$ and $+7H_2O$). With alkali, it gives a 54% yield of phenacyl mercaptan. By (*a*) heating at 119°, (*b*) steam distillation, or, best, (*c*) action of acetic acid on the sodium salt solution at 95—100°, water is eliminated, forming 2-*thion*-4-*phenylthiazoline*-3-*acetic acid*, $PhC⋮CH·S·CS·N·CH_2·CO_2H$; *sodium* salt ($+3\frac{1}{2}H_2O$); *barium* salt ($+2H_2O$ and $+7H_2O$); *methyl* ester, m. p. 115—116°; *ethyl* ester, m. p. 72—73°.

By decomposition of sodium phenacylcarbothiolonglycollate with acetic acid at 80—95°, *phenacyl mercaptan*, $COPh·CH_2·SH$, m. p. 23—24°, b. p. 103°/1·5 mm., 116—118°/4 mm., 140—142°/16—18 mm., n_D^{25} 1·594, d_4^{25} 1·1713, is obtained in 70% yield; *semicarbazone*, m. p. 164—165°; *phenylhydrazone*, m. p. 90—91°; *oxime*, m. p. 70°. It behaves as a pseudo-acid and its *sodium* salt may have the structure $S·CH_2·CPh·ONa$, but only one benzoyl derivative could be obtained. *Phenacyl thiobenzoate*, m. p. 84—85°, was also synthesised from potassium thiobenzoate and phenacyl bromide; *phenylhydrazone*, m. p. 108°. Reduction of the mercaptan by Clemmensen's method gives ethylbenzene. With alcoholic lead acetate, it gives *lead phenacyl sulphide* (gradual decomp.). With phenacyl bromide and sodium ethoxide, *diphenacyl sulphide*, m. p. 77°, is formed. The mercaptan has a simple molecule and does not polymerise, alone or with zinc; condensation products are formed by the action of calcium chloride. Alcoholic hydrochloric acid converts it into 2 : 5-*diphenyl*-1 : 4-*dithiine*, m. p. 118°. This, or phenacyl mercaptan with ethyl mercaptan in presence of hydrochloric acid, gives a condensation product, m. p. 161°, either 2 : 5-*diethylmercapto*-2 : 5-*diphenyl*-1 : 4-*dithiane* or 3 : 6-*diethylmercapto*-2 : 5-*diphenyl*-1 : 4-*dithiane*. Similarly, phenacyl and benzyl mercaptans interact, forming a *compound*, $C_{30}H_{28}S_4$, m. p. 216—217° (on rapid heating) or 206—207° (slow heating). The properties of phenacyl mercaptan are compared with those of hydroxyketones.

In the above experiments, the yield of mercaptan was ascertained by oxidising its solution with iodine in the presence of potassium iodide to *diphenacyl disulphide*, m. p. 81° (yield 90%); *bisphenylhydrazone*, m. p. 150°. When potassium acts on alcoholic diphenacyl disulphide, ether precipitates the *dipotassium* salt, from which acid liberates a *dienol* form, m. p. 168—170° (or 135° on rapid heating); [illegible] derivative, m. p. 168°, is hydrolysed to benzoic acid [illegible] led as bis-β-hydroxystyryl αα′-disulphide. The action [illegible] potassium on alcoholic diphenacyl disulphide gives, after 2 weeks, *diphenacyl*, m. p. 144—145°. The disulphide is more unstable than the mercaptan, sulphur being readily removed by the action of alkali, whilst silver nitrate precipitates silver sulphide. F. M. H.

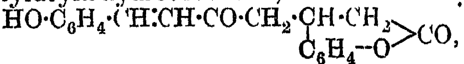
Isomerism of the Styryl Alkyl Ketones. I. Isomerism of 2-Hydroxystyryl Methyl Ketone. A. McGookin and I. M. Heilbron (*J. Chem. Soc.*, 1924, **125**, 2099—2105).—The yellow 2-hydroxystyryl methyl ketone prepared according to Harries (A., 1892, 169) does not condense with gentisaldehyde, but is converted into the colourless isomeride, m. p. 139°, described by Tiemann and Kees (A., 1885, 1074). Protocatechualdehyde, *p*-hydroxybenzaldehyde, or vanillin also brings about the conversion. Vanillin gives a nearly theoretical yield of pure substance. Exposure of an alcoholic solution of the yellow form to the light of a quartz mercury lamp causes complete isomerisation. The colourless isomeride condenses with salicylaldehyde to form 2 : 2′-dihydroxydistyryl ketone, yellow needles, m. p. 159°; Decker and Felser (A., 1908, i, 906) found m. p. 168°. On methylation, 2-methoxystyryl methyl ketone is formed, m. p. 50°, identical with that prepared from the yellow isomeride. The sodium salt was obtained in golden-coloured crystals. An attempt to prepare the sodium salt of the yellow isomeride by treatment of the ketone with alcoholic sodium ethoxide and fractional precipitation of the crimson reaction liquid with chloroform resulted in the separation of (i) lustrous bottle-green crystals of the sodium salt of 2 : 2′-dihydroxydistyryl ketone, (ii) an orange salt, (iii) golden-yellow crystals, and (iv) a pale yellow salt, the sodium derivative of salicylaldehyde. The orange salt is probably the sodium salt of the yellow isomeride, although on dissolving in water and acidifying the solution only the colourless isomeride was obtained. The oxime, semicarbazone, and phenylhydrazone of the colourless ketone are identical with those obtained from the yellow isomeride. The isomerism is considered to be of the *cis-trans* type, the yellow isomeride being the *cis*-form. It is the more labile and tends to disrupt in presence of alkali. In all cases where isomeric styryl ketones have been obtained the isomerides have identical m. p., and one form appears to pass into the other at or just below the m. p. The colourless isomerides of 5-bromo-2-hydroxystyryl methyl ketone and 3-methoxy-4-hydroxystyryl methyl ketone were prepared from the yellow forms by methods similar to the above. The yellow form of 4 : 5-methylenedioxystyryl methyl ketone, m. p. 107° (Haber, A., 1891, 704), on purification had m. p. 110—111°, identical with that of the colourless variety. A. C.

Interaction of Ethyl Acetoacetate and *o*-Hydroxydistyryl Ketones. I. M. Heilbron and T. A. Forster (*J. Chem. Soc.*, 1924, **125**, 2064—2068; cf. this vol., i, 413).—3-o-*Hydroxyphenyl*-5-o-*hydroxystyryl*-Δ^5-cyclo*hexen*-1-*one*,



$$\begin{array}{l} \qquad\qquad\quad CH_2\cdot CO\cdot CH \\ OH\cdot C_6H_4\cdot CH\cdot CH_2\cdot C\cdot CH{:}CH\cdot C_6H_4\cdot OH \end{array} \qquad (I.),$$

m. p. 240° (with 1 mol. of methyl alcohol), was prepared by condensing 2 : 2′-dihydroxydistyryl ketone with ethyl acetoacetate in aqueous sodium hydroxide solution. It was accompanied by 4-*o*-hydroxystyracyldihydrocoumarin,



$$HO{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_2{\cdot}\underset{C_6H_4-O}{CH}{\cdot}CH_2>CO,$$

m. p. 235°, *methyl ether*, m p 130°. The hexenone gives a deep red, the coumarin only a pale yellow coloration with concentrated sulphuric acid. 3-o-*Methoxyphenyl*-5-o-*methoxystyryl*-Δ^5-cyclo*hexen*-1-*one*, m. p. 128°, was obtained on methylating the corresponding dihydroxy*cyclo*hexenone. 2 : 2′-*Dimethoxydistyryl ketone*, m. p. 127°, condenses with sodium ethyl acetoacetate in boiling alcohol forming *ethyl* 3-o-*methoxyphenyl*-5-o-*methoxystyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, m. p. 159°. The carbethoxy group could not be removed by either acid or alkali. 3-o-*Hydroxyphenyl*-5-o-*methoxystyryl*-Δ^5-cyclo*hexen*-1-*one*, m. p. 172°, was similarly prepared from 2′-methoxy-2-hydroxydistyryl ketone Its methyl ether is identical with the dimethyl ether of I. *Ethyl* 3-o-*methoxyphenyl*-5-o-*hydroxystyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate*, m. p. 159—161°, was obtained from the alkaline filtrate of the above hexenone. 2-*Acetyl*-3-o-*methoxyphenyl*-5-o-*methoxystyryl*-Δ^5-cyclo*hexen*-1-*one*, m. p 174°, was prepared by condensing 2 : 2′-dimethoxydistyryl ketone with acetylacetone. On heating it with a mixture of potassium methoxide and hypoiodite, the acetyl group was split off and a methyl ether obtained identical with that from I. A. C.

Chalkones and Hydrochalkones. V. TOGNAZZI (*Gazzetta*, 1924, **54**, 697—704; cf. Bargellini, A., 1912, i, 118; 1913, i, 59, 90; 1914, i, 1074; 1915, i, 19).—When reduced by means of hydrogen in presence of platinum or palladium black, chalkones usually undergo hydrogenation at the double linking, but not at the carbonyl group, the only two known exceptions to this rule being 2 : 4 : 6-trimethoxyphenyl 3 : 4-dimethoxystyryl ketone, which yields 2 : 4 : 6 : 3′ : 4′-pentamethoxy-αγ-diphenylpropane, and 4 : 6-dimethoxy-2-ethoxyphenyl 3 : 4-dimethoxystyryl ketone, which also yields the corresponding propane derivative (cf. Freudenberg, A., 1920, i, 752). Of a number of other chalkones examined by the author, only one, namely, furfurylidene-2 : 4 : 5-trimethoxyacetophenone, appears to absorb more than 2 atoms of hydrogen per molecule, but the product of the reaction was resinous and could not be purified. Certain compounds analogous to the chalkones, such as distyryl ketone, also seem to absorb, in presence of platinum black, more hydrogen than is required by the double linkings.

p-*Methoxyphenyl* p-*methoxystyryl ketone* (4 : 4′-*dimethoxychalkone*), prepared from anisaldehyde and *p*-methoxyacetophenone, has m. p. 100—102°, and p-*methoxyphenyl* β-p-*methoxyphenylethyl ketone* has m. p. 29—31°.

4′-*Methoxy*-3 : 4-*dioxymethylenechalkone* [p-*anisyl piperonylidenemethyl ketone*], from *p*-methoxyacetophenone and piperonaldehyde (cf. Scholtz and Meyer, A., 1910, i, 562), gives p-*anisyl piperionylethyl ketone*, $C_{17}H_{16}O_4$, m. p. 56—58°, on reduction in presence of platinum black.

p-*Anisyl furfurylidenemethyl ketone*, $OMe\cdot C_6H_4\cdot CO\cdot CH{:}CH\cdot C_4H_3O$, from *p*-methoxyacetophenone and furfuraldehyde, m. p. 79—81°, yields an oily reduction product. 2 : 4 : 5-*Trimethoxyphenyl furfurylidenemethyl ketone* has m. p. 116—118°.

2-Hydroxy-4-methoxyphenyl piperonylidenemethyl ketone (piperonalpaeonol; cf. Emilewicz and von Kostanecki, A., 1899, i, 368) gives 2-*hydroxy*-4-*methoxyphenyl piperonylethyl ketone*, $C_{17}H_{16}O_5$, white needles, m. p. 85—87°, on reduction.

2′ : 4′ : 5′-Trimethoxy-3 : 4-dioxymethylenechalkone has m. p. 186—188° (cf. Bargellini and Avrutin, A., 1911, i, 68), and 2 : 4 : 5-*trimethoxyphenyl piperonylethyl ketone*, $C_{19}H_{20}O_6$, has m. p. 131—133°. T. H. P.

Functions of Chromophores. X. The Quinone Chromophore. II. J. Lifschitz [with J. Zimmermann, H. Lourié, and G. A. Ten Bokkel-Huinink] (*Rec. trav. chim.*, 1924, **43**, 403—419).—All groups which contain a cross-conjugated system of unsaturated linkings may be regarded as quinonoid chromophores. This structure, rather than its diketonic nature, determines the chromophoric character of the quinone in the narrow sense; the central carbon atom is the source of the colour. This conception permits of a single explanation of the optical properties of dyes and their relationship to the quinones (cf. this vol., i, 654).

H. J. E.

Functions of Chromophores. XI. The Quinone Chromophore. III. J. Lifschitz (*Rec. trav. chim.*, 1924, **43**, 654—670).—The views previously developed (this vol., i, 654 and preceding abstract) on the subject of the *p*-quinone chromophore are successfully applied in the discussion of the molecular compounds of quinone, the halochromism of triphenylmethane derivatives and ketones and of free radicals. The views of earlier workers in these fields are critically discussed. W. E. E.

Colour of the Simple Quinoneimines and their Salts. II. Some New Quinoneimines and their Stability. B. Cordone (*Helv. Chim. Acta*, 1924, **7**, 956—964; cf. this vol., i, 214).—Quinoneimines are particularly prone to two reactions and, according to circumstances, one of the two is generally favoured to the exclusion of the other. Hydrolysis to the corresponding quinone in presence of water is slow at the ordinary temperature, but at the boiling point the action is rapid and quantitative. The more heavily the nucleus is substituted by alkyl groups, the more rapid is the hydrolysis. The tendency to polymerise is affected by light, temperature, and the presence of acids, but chiefly by the number of substituent alkyl groups. The presence of even a single alkyl group in the nucleus of a quinoneimine will greatly lessen its tendency to polymerise, particularly if it is adjacent to the imino group. The effect of acids varies. In ether solution, and more especially in the dry state, anhydrous acids cause polymerisation. The tendency of the quinoneimine bases to "quinonise" in the presence of water is changed by acid to a tendency to polymerise.

On the other hand, homologues of benzoquinoneimines containing in the nucleus at least two alkyl groups and hence possessing relatively little tendency to polymerise are caused to "quinonise" by mineral acids in aqueous solution. The hydrochlorides undergo this change more easily than the sulphates. The picrates of the quinoneimines polymerise like the free bases, but more slowly: picric acid has no hydrolysing effect, but retards condensation. *Thymoquinonedi-imine* is obtained in ethereal solution by oxidising *p*-diaminocymene with silver oxide; the *monopicrate* exists in a yellow and a red form. In aqueous solution, the sulphate and the chloride readily form the quinone. The sulphate liberates iodine from potassium iodide. Toluquinone-2-imine, from *p*-amino-*m*-cresol, is easily isolated and may be preserved for a long time. The monopicrate (two forms) is more stable than the base. No other mono-salt is obtainable, but the yellow solution of the di-salt in concentrated sulphuric acid is stable. The aqueous solution of the base is stable unless heated, when the quinone is formed. Toluquinone-3-imine, from *p*-amino-*o*-cresol, is too unstable to be isolated. All the mono-salts polymerise immediately except the picrate, which exists in a yellow, amorphous form and a dense, red, crystalline form. W. E. E.

Colour and Constitution. IX. F. KEHRMANN (*Helv. chim. Acta*, 1924, 7, 964—968; cf. A., 1922, ii, 333).—In view of Piccard's observation (A., 1913, i, 895) that certain quinonedi-imines, particularly the oxidation product of *p*-dimethylaminodiphenylamine, give di-salts lighter in colour than their mono-salts, the rule previously formulated must be modified to this: "If the unsaturation persists after salt formation, the addition of acids to unsaturated groupings results most frequently in a deepening of colour, even if tervalent nitrogen becomes quinquevalent. This deepening occurs regularly if the chromophore is open to the attack of the acid only at one point. When two basic groups are present, the neutralisation of the first leads to a deepening, whilst that of the second may, exceptionally, cause a lightening of the colour."

The mono-salts of the quinonedi-imines under discussion are reddish-violet, the di-salts reddish-orange; Piccard's observations on the colour of these salts are incorrect. W. E. E.

Derivatives of Arylaminomercaptonaphthaquinones. FARBWERKE VORM. MEISTER, LUCIUS, UND BRÜNING (D.R.-P. 386998; from *Chem. Zentr.*, 1924, i, 2634).—The derivatives are prepared by treating 3-chloro-2-arylamino-1 : 4-naphthaquinone derivatives with alkali sulphides. Thus, 3-*chloro*-2-*anilino*-1 : 4-*naphthaquinone* (from 2 : 3-dichloro-1 : 4-naphthaquinone and aniline) is boiled for a short time with sodium sulphide to give a blue solution of the *sodium* salt of 2-*anilino*-3-*mercapto*-1 : 4-*naphthaquinone*, from which hydrochloric acid precipitates the dark violet *mercaptan*, which is converted by atmospheric oxidation into *benzonaphthophenthiazinequinone*. On heating 2 : 3-dichloro-1 : 4-naphthaquinone with aceto-*p*-phenylenediamine, 3-*chloro*-2-p-*acetamido*-

phenylamino-1 : 4-*naphthaquinone* is obtained as red crystals, m. p. 271° ; this yields the corresponding *mercapto* compound, which is oxidised by the air to the corresponding green p-*thiazine* ; this is further oxidised by hydrogen peroxide to the brownish-red *sulphoxide* of an *acetamidobenzonaphthoparathiazinequinone*.

F. A. M.

Photochemical Behaviour of Methylanthraquinones. A. Schaarschmidt and K. Kasai (*Ber.*, 1924, **57**, [*B*], 1671—1673).— Methylanthraquinones may be arranged in the following order of decreasing sensitiveness towards light : 4-chloro-1-methylanthraquinone, 2-methylanthraquinone, 3-bromo-2-methylanthraquinone, 1-nitro-2-methylanthraquinone, 1-methylanthraquinone, 3-chloro-2-methylanthraquinone, 1-chloro-2-methylanthraquinone, 1-chloro-2-dibromomethylanthraquinone, 1 : 3-dimethylanthraquinone. 1 : 3-Dimethylbenzophenone is not appreciably altered by exposure to light. Since 4-chloro-1-methylanthraquinone becomes similarly altered when illuminated in an atmosphere of nitrogen or in a high vacuum, the change is considered to consist in a transformation into a coloured quinonoid modification which is not completely converted into the original form when rapidly crystallised from alcohol.

H. W.

Tetrahydroxydimethylanthraquinone. G. Flumiani (*Monatsh.*, 1924, **45**, 43—49).—Two compounds prepared by Brunner (*ibid.*, 1881, **2**, 466) are shown to be 1 : 4 : 5 : 8-tetrahydroxy-2 : 6-dimethylanthraquinone and 2 : 6-dimethylanthracene. Brunner's starting point is now recognised as 3 : 6-dihydroxy-*p*-toluic acid (Schmid, A., 1911, i, 780 ; Herrmann, A., 1877, ii, 319 ; Baeyer, A., 1886, 445). By treatment with concentrated sulphuric acid at 120—130°, it gives a heterogeneous solid which after many recrystallisations from ethyl benzoate yields 1 : 4 : 5 : 8-*tetrahydroxy*-2 : 6-*dimethylanthraquinone*, a red powder; when heated slowly it sinters at 200° and sublimes, with slight charring, from 260°; on rapid heating, m. p. 290—300° with sublimation. Benzoic anhydride at 130—135° converted it into a *dibenzoyl* derivative, white needles, m. p. 220°. Boiling acetic anhydride, with sodium acetate, formed the *tetra-acetyl* derivative, m. p. 235—236° (yield 50%). Distillation of the tetrahydroxy compound with zinc dust in a current of hydrogen gave 2 : 6-*dimethylanthracene* (yield 20%); m. p. 242—243°, after many recrystallisations. This is oxidised by chromic acid in acetic acid solution to 2 : 6-dimethylanthraquinone.

F. M. H.

Formulæ of Dicyclic Terpenes. C. Slawinski (*Bull. Soc. chim.*, 1924, [iv], **35**, 1195—1198).—The formulæ proposed for the dicyclic terpenes by Dupont (A., 1922, i, 1042) involve two new conceptions of oscillating bonds and the linking of three valencies of three separate carbon atoms with the " bridge " carbon atom, which introduce fresh complications. The author contends that his extended theory of conjugated bonds (cf. A., 1899, i, 529) is sufficient to explain the transformations of these terpenes. R. B.

Chemistry of Cadinene. I. G. G. HENDERSON and A. ROBERTSON (*J. Chem. Soc.*, 1924, **125**, 1992—1996).—Cadinene of greater purity than 70% could not be obtained by the repeated fractional distillation under reduced pressure of oil of cubebs. The fraction of b. p. 125—140°/12 mm. was mixed with glacial acetic acid (⅓ vol.) and cadinene precipitated as the hydrochloride. Pure cadinene was obtained from the latter by means of anhydrous sodium acetate. Agitation of a solution of cadinene hydrochloride in glacial acetic acid with silver acetate at 70° resulted in the formation of a light yellow oil, which was steam-distilled, and a saturated *compound*, $C_{15}H_{28}O_2$, m. p. 194—195°, probably a glycol, was isolated from the residue in 2% yield. The volatile portion consisted of cadinene and an unsaturated *compound*, $C_{15}H_{25}OH$, apparently the alcohol cadinol (cf. Semmler and Jonas, A., 1915, i, 63). It formed a *bromo-dibromide*, $C_{15}H_{25}OBr_3$, an unstable, oily liquid. These hydroxy compounds were not obtained when cadinene hydrochloride was treated with silver acetate in ethereal or alcoholic solution, the sole product being cadinene. Cadinene was not hydrated by heating its acetic acid solution with 30% sulphuric acid, but yielded a brown oil the greater part of which was volatile in steam and consisted of an isomeric unsaturated hydrocarbon, termed iso*cadinene*, b. p. 125—128°/12 mm., d_4^{20} 0·9160, n_D^{20} 1·5141. The same substance was obtained on heating cadinene with glacial acetic acid at 230—235° for 24 hours. It had [α] −1·0°, quickly resinified in air, absorbed bromine with evolution of hydrogen bromide, and formed no solid nitrosochloride, nitrosite, or nitrosate. A sesquiterpene was isolated from the liquid left after isolating cadinene hydrochloride from oil of cade which appears very similar to one described by Lepeschkin (A., 1908, i, 278). A. C.

Essential Oil of *Backhousia angustifolia*. I. A. R. PENFOLD (*J. Proc. Roy. Soc. N.S. Wales*, 1923, 57, 300—312).—The oil, obtained in a yield of 1·08% by steam-distillation of the leaves and terminal branchlets, contains 75% of a hitherto undescribed *phenol* ($C_{10}H_{14}O_3$, b. p. 122—124°/10 mm.) of poor germicidal value, together with *d*-α-pinene, β-pinene, cineol, alcoholic compounds (*e.g.*, α-terpineol), a sesquiterpene, and a stearoptene ($C_{15}H_{16}O_5$; probably a lactone) of m. p. 118—119°. The phenol is an almost colourless, viscous liquid, giving a brilliant orange-red coloration with alcoholic ferric chloride. It forms a crystalline *ammonium* derivative, $C_{10}H_{17}O_3N$, m. p. 135—137°, and a purple, crystalline *copper* derivative, $(C_{10}H_{12}O_3)_2Cu$, m. p. 193—194°. Oxidation of the phenol with alkaline potassium permanganate gives potassium acetate and potassium carbonate. W. T. K. B.

Essential Oil of *Darwinia grandiflora* and the Presence of a New Acetic Ester. A. R. PENFOLD (*J. Proc. Roy. Soc. N.S. Wales*, 1923, 57, 237—248).—Distillation of the leaves and terminal branchlets of *Darwinia grandiflora* yields a mobile, pale yellow oil ([illegible]%), the main constituents of which are *d*-α-pinene, an [illegible]ified terpene (b. p. 175—177°), an acetic ester ($C_{10}H_{18}O$; [illegible] 108—116°/10 mm.) named *darwinol acetate* and not hitherto described, a sesquiterpene (b. p. 130—133°/10 mm.; possibly identical with eudesmene) and corresponding sesquiterpene alcohol (b. p. 134—138°/5 mm.), a stearoptene (m. p. 103—104°; probably a phenol ether), and small quantities of *iso*valeraldehyde, amyl alcohol, and an ester. W. T. K. B.

Essential Oils of *Callistemon lanceolatus* and *C. viminalis*. A. R. Penfold (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 131—139).—The essential oil of *Callistemon lanceolatus*, obtained in a yield of 0·06—0·22%, contains cineol, dipentene, limonene, terpineol, sesquiterpene, and a small amount of phenols. *C. viminalis* appears to exist in two varieties, that from New South Wales yielding an oil (0·13—0·22%) containing *d*-α-pinene, cineol (about 30%), phenol (2%), sesquiterpene, and probably terpineol, whilst the oil from the Queensland variety (0·21—0·22%) contains cineol (60—80%), dipentene, limonene, terpineol, sesquiterpene, and phenol (about 0·5%). W. T. K. B.

Germicidal Values of Commercial Eucalyptus Oils and their Pure Constituents, with Observations on the Value of Concentrated Disinfectants. A. R. Penfold and R. Grant (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 80—89).—The Rideal-Walker coefficients of a number of eucalyptus oils and their chemically pure constituents are tabulated. Terpenes (*e.g.*, pinene, phellandrene, limonene), sesquiterpenes, and sesquiterpene alcohols possess poor germicidal properties, whilst ketones (piperitone type), alcohols (piperitol and geraniol types), aromatic and open-chain aldehydes (cuminal, citral, and citronellal types), and phenols (*e.g.*, australol) possess well-marked germicidal properties. The effect of dilution on the coefficient of various germicidal preparations, including those with tar oils and phenol, is discussed, and it is shown that the germicidal value of a disinfectant is greater the greater the initial dispersion, provided dilution is made when the soap solution is added. W. T. K. B.

Germicidal Values of Australian Essential Oils (exclusive of Eucalypts) and their Pure Constituents, together with those of some Essential Oil Isolates and Synthetics. I. A. R. Penfold and R. Grant (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 211—215; cf. preceding abstract).—The Rideal-Walker coefficients of the above are tabulated. Of the crude oils examined that from *Backhousia citriodora* has the highest coefficient (16; principal active constituent, citral) and that from *Homoranthus virgatus* the lowest (1; principal active constituent, *d*-α-pinene). Of the pure constituents thymol has the highest coefficient (25) and leptospermol the lowest (<1). W. T. K. B.

Constitution of Lichenol. A. S. Pfau (*Parfums de France*, 1924, No. 16, 137).—The compound, lichenol, m. p. 72—73°, found by Gattefossé (*Parfumerie moderne*, 1911, **4**, 6) to be the chief constituent of oak moss (*Evernia prunastri*, Ach.) oil, has m. p. 73·5—74° and is identical with ethyl evernate (Pfau, this vol., i, 512). Chemical Abstracts.

Isoprene and Caoutchouc. VII. Homologues of Hydrocaoutchouc. H. STAUDINGER and W. WIDMER (*Helv. Chim. Acta*, 1924, 7, 842—848; cf. A., 1922, i, 1043).—The hydrohalides of caoutchouc are colloids which very readily lose hydrogen halide. To explain this, however, no special hypothesis is needed (cf. Pummerer and Burkhard, A., 1923, i, 49), the hydrohalides being regarded as hydrocaoutchouc, in which the tertiary hydrogen atom is substituted by halogen. Caoutchouc hydrobromide does not react with magnesium alkyl iodide, but with zinc dimethyl and zinc diethyl, methyl- and ethyl-hydrocaoutchouc, respectively, are easily obtained. Unless the reaction mixture is well cooled, the homologue is in both cases contaminated with a saturated isomeride of caoutchouc formed by ring closure after loss of methane (or ethane) and hydrogen halide. The new homologues of hydrocaoutchouc possess essentially the same physical and chemical properties as the parent. Above all, they are colloids. As paraffin hydrocarbons, they are stable towards permanganate, nitric acid, and bromine. They resemble hydrocaoutchouc in giving, on heating, fission products of olefinic character. The previous observation that saturated hydrocarbons may be colloids is confirmed. Together with its chemical properties, the colloidal nature of hydrocaoutchouc is direct evidence in favour of the new conception of the structure of caoutchouc (A., 1922, i, 1043). Harries (A., 1923, i, 693) has asserted that the action of high-pressure hydrogen on caoutchouc at 270° gives pyrogenic decomposition products. This cannot be true, however, because pyrogenic decomposition of caoutchouc gives molecular disperse decomposition products, which would yield, on reduction, molecular disperse reduction products. Harries' objection is further vitiated by the low-temperature transformation of caoutchouc into the colloidal homologues of hydrocaoutchouc.

W. E. E.

Synthesis of Amygdalin. R. KUHN and H. SOBOTKA (*Ber.*, 1924, 57, [*B*], 1767—1769).—Bromoacetogentiobiose is converted by ethyl *dl*-mandelate and silver oxide into a mixture of ethyl *d*-hepta-acetylamygdalate, m. p. 212·5—213·5° (corr.), $[\alpha]^{20}_{D}$ —72·8° in chloroform, and ethyl *l*-hepta-acetylamygdalate, m. p. 189·5—191° (corr.), which are separated from one another by fractional crystallisation from methyl and ethyl alcohols. The same products are obtained by hydrolysing amygdalin with barium hydroxide solution, converting the *dl*-amygdalic acid thus produced into its ethyl ester, and acetylation of the latter substance.

The compound described by Campbell and Haworth (T., 1924, **125**, 1337) as ethyl *dl*-hepta-acetylamygdalate is a derivative of *d*-mandelic acid.

In contrast to the previous practice, natural amygdalin, prunasin, and their derivatives which yield lævorotatory mandelic acid when hydrolysed are described as *d*-derivatives, since Freudenberg, Brauns, and Siegel (A., 1923, i, 215) have established the position of lævorotatory mandelic acid among the *d*-α-hydroxy-acids.

H. W.

Strophanthin. V. Isomerisation and Oxidation of *iso*-Strophanthidin. W. A. Jacobs and A. M. Collins (*J. Biol. Chem.*, 1924, **61**, 387—403; cf. A., 1923, i, 123; this vol., i, 65, 867).—When strophanthidin is treated with cold methyl-alcoholic potassium hydroxide, it is converted quantitatively into α-*iso*-strophanthidin, m. p. 255—257°, $[\alpha]_D^{22}$ −34° in methyl alcohol, which is precipitated on pouring the solution into water; more of the substance can be obtained by warming the mother-liquor after acidification to Congo-red. Unlike strophanthidin, it cannot be reduced with hydrogen and palladium, which suggests that isomerisation may involve a shift in the ethylenic linking. It gives an *oxime*, m. p. 236°, which can also be obtained by the action of methyl-alcoholic potassium hydroxide on strophanthidinoxime. On oxidation with sodium hypobromite, α-*iso*strophanthidin gives a mixture of two monobasic, lactonic acids. The greater part of the product is α-iso*strophanthidic acid*, $C_{23}H_{32}O_7$, leaflets with $1H_2O$, m. p. 231—233°, $[\alpha]_D^{23}$ −16·3° in 95% alcohol; the *methyl* ester has a variable melting point, $[\alpha]_D^{20}$ −15° in chloroform; the *benzoate* of the methyl ester has m. p. 230°; the *oxime* of the methyl ester, m. p. 263°. The other *acid*, $C_{23}H_{30}O_7$, was separated by means of its sparingly soluble ammonium salt; it forms needles with $0{\cdot}5H_2O$, m. p. 230°, or anhydrous leaflets, m. p. 254—257°, from hot alcohol; $[\alpha]_D^{23}$ −69° in 95% alcohol. On boiling with sodium hydroxide, the lactone group is hydrolysed with the formation of a dibasic *acid*, $C_{23}H_{32}O_8$, flat needles with $1{\cdot}5H_2O$, m. p. 183°. The *methyl* ester of the lactonic acid has m. p. 253—256°, $[\alpha]_D^{4}$ −59·5° in chloroform, and does not form a benzoate or an oxime. On oxidation in ammoniacal solution with potassium permanganate (1 mol. of oxygen), α-*iso*-strophanthidic acid gives a dibasic acid, $C_{23}H_{32}O_8$, α-iso*strophanthic acid*, which forms platelets with $1H_2O$, m. p. 232—234°, $[\alpha]_D^{20}$ −8° in methyl alcohol. On heating, this acid loses 1 mol. of carbon dioxide. It can also be obtained directly from *iso*strophanthidin by oxidation in alkaline solution with permanganate (2 mols. of oxygen). The *dimethyl* ester has m. p. 224—225°, $[\alpha]_D^{25}$ −12° in chloroform; the *benzoate* of the dimethyl ester has m. p. 201—203°.

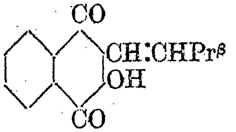
When α-*iso*strophanthidic acid is boiled with dilute sodium hydroxide and then oxidised with permanganate (1 mol. of oxygen) the product consists of a mixture of α-*iso*strophanthic acid and a second isomeric acid which forms needles, m. p. 277—279°, $[\alpha]_D^{25}$ −26° in methyl alcohol, and is identical with the strophanthic acid previously obtained by the oxidation of strophanthidin (this vol., i, 65) and erroneously given the formula $C_{23}H_{30}O_8$. It is now called β-iso*strophanthic acid* and appears to be a stereoisomeride of the α-compound. The strophanthic acid of Feist (A., 1900, i, 555) was probably a mixture of α- and β-*iso*strophanthic acids.

C. R. H.

Constitution of Santonin. A. Angeli (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 10—16).—A reprint of work already published (A., 1907, i, 321; 1908, i, 543).

T. H. P.

Mangostin, the Yellow Colouring Matter of the Rind of the Fruit of *Garcinia mangostana*. J. Dekker (*Rec. trav. chim.*, 1924, **43**, 727—730).—By crystallising from benzene the mixture of colouring matter and resin obtained by extracting the rind with alcohol, mangostin, $C_{16}H_{16}O_4$, is obtained in bright yellow needles, m. p. 176·5—177°. Fusion with alkali gives a product which has the odour of amyl alcohol but, after acidification, of valeric acid. Hence mangostin is possibly methoxyhydroxylapachol (lapachol has the annexed formula; cf. A., 1906, i, 873).



The presence of one methoxyl group is indicated, and the coloration which mangostin gives with ferric chloride points to the presence of a hydroxyl group. Methylation gives *methylmangostin*, yellow crystals, m. p. 122·5—123°, which contains two methoxyl groups and gives a colourless *acetyl* derivative, m. p. 196°. The mangostin obtained in this investigation does not reduce gold and platinum salts; hence the products of Schmid (*Annalen*, 1855, **93**, 83) and of Liechti (*Diss.*, Bern, 1891), which did so, were probably impure. W. E. E.

Preliminary Experiments on Feather Pigments. W. D. Bancroft (*J. Physical Chem.*, 1924, **28**, 1147—1150).—The red and yellow feather pigments which are or are not easily extracted by alcohol are respectively not fast or fairly fast to light. The solutions in all cases are yellow. The extracted pigment behaves like an acid dye, *i.e.*, it does not dye cotton direct and dyes wool more strongly from an acid than from an alkaline bath. It is adsorbed by alumina. M. B. D.

Pyrylium Compounds. XIII. Reactivity of Methyl Groups in the α- and γ-Positions in Pyrylium Salts. W. Dilthey and J. Fischer (*Ber.*, 1924, **57**, [*B*], 1653—1656; cf. Dilthey, A., 1923, i, 699; Buck and Heilbron, T., 1923, **123**, 1395, 2521).—The reactivity of methyl groups in the α- and γ-positions in pyrylium salts is established by their ability to react with aromatic aldehydes. The following salts are thus derived from 4 : 6-diphenyl-2-methylpyrylium compounds: 4 : 6-*diphenyl*-2-*styrylpyrylium perchlorate*, m. p. 235°; 4 : 6-*diphenyl*-2-p-*methoxystyrylpyrylium perchlorate*, m. p. 228—229°, and the additive *compound* of the chloride with ferric chloride, m. p. 198°; 4 : 6-*diphenyl*-2 : 4′-*hydroxystyrylpyrylium perchlorate*, m. p. 254°, and the *ferric* compound, m. p. 172°; 4 : 6-*diphenyl*-2 : 2′-*hydroxystyrylpyrylium perchlorate*, m. p. 248°, and the *ferric* salt, m. p. 174°; 4 : 6-*diphenyl*-2-β-*styrylvinylpyrylium perchlorate*, m. p. 255°, and the *ferric* compound, m. p. 236°. 2 : 6-Diphenyl-4-methylpyrylium salts yield the following compounds: 2 : 6-*diphenyl*-4-*styrylpyrylium perchlorate*, m. p. 254—255°; 2 : 6-*diphenyl*-4-p-*methoxystyrylpyrylium perchlorate*, m. p. 272°; 2 : 6-*diphenyl*-4-p-*hydroxystyrylpyrylium perchlorate*, m. p. 265°; 2 : 6-*diphenyl*-4-o-*hydroxystyrylpyrylium perchlorate*, m. p. 243—244°; 2 : 6-*diphenyl*-4-β-*styrylvinylpyrylium perchlorate*, m. p. 240°.

In reply to Schneider and Ross (A., 1923, i, 1111), it is admitted that the formation of 4 : 6-diphenyl-2-methylpyrylium salts from acetophenone and acetic anhydride may occur through the intermediate formation of dypnone, but experimental evidence is adduced in favour of the view that benzoylacetone is more probably an intermediate product. H. W.

Sulphur as the Bridge Atom in the Middle Ring of some Anthracene Derivatives. A. Bistrzycki and A. Traub (*Helv. Chim. Acta*, 1924, 7, 935—944; cf. A., 1922, i, 268).—In warm glacial acetic acid solution, hydrogen chloride causes *p*-tolualdehyde and thiobenzilic acid to condense almost quantitatively to give 4 : 4-*diphenyl*-2-p-*tolyl*-1 : 3-*oxthiophan*-5-*one*, prisms, m. p. 100—100·5°. Sulphuric acid converts this substance into 9-*phenyl*-2-*methyl*-9 : 10-*dihydro*meso*thioanthracene*, greenish-yellow needles, m. p. 99·5—100·5°. Neither alcoholic phenylhydrazine nor boiling 10% alcoholic sodium hydroxide solution affects the substance, so that the sulphur cannot be bound as in a thioketone. Distilled with zinc dust under the conditions in which phenyldihydro*meso*thioanthracene gives phenylanthracene, the present substance gives no solid product. At a higher temperature 2-methylanthracene is obtained.

Reduction in glacial acetic acid solution by zinc dust and hydrochloric acid gives 1-*phenyl*-3-p-*tolylthiophthalan*, needles, m. p. 103—104°. Oxidation in boiling glacial acetic acid solution by 4% potassium permanganate solution yields 2-*p*-toluoylbenzophenone. The condensation of thiobenzilic acid and cuminaldehyde gives 4 : 4-*diphenyl*-2-*cumenyl*-1 : 3-*oxthiophan*-5-*one*, m. p. 100—100·5°. From *o*-chlorobenzaldehyde 4 : 4-*diphenyl*-2-o-*chlorophenyl*-1 : 3-*oxthiophan*-5-*one*, m. p. 105·5°, is obtained, and is converted by sulphuric acid into 4-*chloro*-9-*phenyl*-9 : 10-*dihydro*meso*thioanthracene*, green prisms, showing marked triboluminescence, m. p. 89°. Alcoholic ammonium hydroxide at 220—230° has no action on this compound. *m*-Chlorobenzaldehyde gives (quantitatively) 4 : 4-*diphenyl*-2-m-*chlorophenyl*-1 : 3-*oxthiophan*-5-*one* (m. p. 83—84°), and thence (probably) 3-*chloro*-9-*phenyl*-9 : 10-*dihydromesothioanthracene* (m. p. 102—103·5°). Whilst 2-*o*-nitrophenyl-4 : 4-diphenyl-1 : 3-oxthiophan-5-one could not be converted into an anthracene derivative, 2-*m*-nitrophenyl-4 : 4-diphenyl-1 : 3-oxthiophan-5-one gives 3-*nitro*-9-*phenyl*-9 : 10-*dihydro*meso*thioanthracene* (m. p. 151° indef., depending on rate of heating). The following condensation products of thiobenzilic acid are all obtained in good yield by the usual method, but they do not give the corresponding *meso*thioanthracene derivatives: 4 : 4-*diphenyl*-2-p-*nitrophenyl*-1 : 3-*oxthiophan*-5-*one* (m. p. 148°), 4 : 4-*diphenyl*-2-p-*dimethylaminophenyl*-1 : 3-*oxthiophan*-5-*one* (m. p. 124° decomp.), 4 : 4-*diphenyl*-2-(mp-*methylenedioxyphenyl*)-1 : 3-*oxthiophan*-5-*one* (m. p. 119·5°), 1 : 4-*di*-2(5-*keto*-4 : 4-*diphenyltrihydro*-1 : 3-*oxthienyl*)*benzene* (m. p. 195—196°). W. E. E.

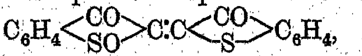
Naphthathioindoxyls. R. Tobler, R. Stocker, J. Müller, and A. Bucher (U.S. Pat. 1492054).—Treatment of thionaphthoisatin compounds in alkaline solution with a monohalogen acid, elimination of carbon monoxide, and ring closure by condensation yields naphthothioindoxyls. The following compounds are mentioned: *Naphthalene-1-thioglyoxylic acid*, m. p. 171—172°; *naphthalene-1-thioglycol-2-carboxylic acid*, m. p. 144—145°; 1 : 2-*naphthothioindoxyl*; 2 : 1-*naphthothioindoxyl*; 4-*chloro*-1 : 2-*naphthothioindoxyl*, m. p. 165° (5-*chloro*-, m. p. 176°); 5-*chloro*-2 : 1-*naphthothioindoxyl*, m. p. 146° (5-*bromo*-, m. p. 170°; 8-*chloro*-, m. p. 179°; 7-*chloro*-, m. p. 155°); 1-*chloro*-2 : 3-*naphthothioindoxyl* (*acetyl* derivative, m. p. 106°); 1-*bromo*-2 : 3-*naphthothioindoxyl*, m. p. 155°.

Chemical Abstracts.

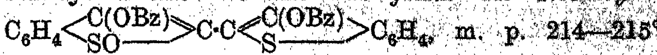
Indigotin Group. V. Derivatives of "Thioindigo." T. Posner and E. Wallis (*Ber.*, 1924, **57**, [*B*], 1673—1681; cf. Posner and Heumann, A., 1923, i, 953; Posner and Kemper, this vol., i, 1237).—The assumption made previously that the action of nitrous fumes on indigotin results in the replacement of the imino-hydrogen atoms by the nitroso group is confirmed indirectly by the observation that bisoxythionaphthen is only slowly attacked by this reagent, whereby it is converted into thionaphthenquinone,

$C_6H_4<\genfrac{}{}{0pt}{}{CO}{S}>CO$, m. p. 121°.

Bisoxythionaphthen is slowly oxidised by nitric acid (*d* 1·4) at the atmospheric temperature to the corresponding *monosulphoxide*,

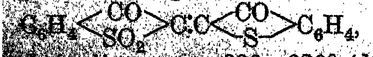


$C_6H_4<\genfrac{}{}{0pt}{}{CO}{SO}>C:C<\genfrac{}{}{0pt}{}{CO}{S}>C_6H_4$, m. p. above 300°, which appears to be identical with the substance described by Bezdrik, Friedländer, and Koeniger (A., 1908, i, 200), and by Danaila (A., 1910, i, 411). The compound is readily reduced by sodium hyposulphite and sodium hydroxide to the dihydro substance, which, however, is oxidised by air to bisoxythionaphthen. Addition of benzoyl chloride to the vat yields the *dibenzoyl* derivative,



$C_6H_4<\genfrac{}{}{0pt}{}{C(OBz)}{SO}>C\cdot C<\genfrac{}{}{0pt}{}{C(OBz)}{S}>C_6H_4$, m. p. 214—215°, whereas the action of benzoyl chloride on the sulphoxide in the presence of boiling pyridine leads to the production of 3 : 3′-*bisbenzoxythionaphthen*, m. p. 226°, which is also prepared by the action of benzoyl chloride on the hyposulphite vat from bisoxythionaphthen or on the latter dissolved in boiling pyridine. The sulphoxide is transformed by reductive acetylation with acetic anhydride into 3 : 3′-*bisacetoxythionaphthen*, m. p. 240°, which is obtained similarly from bisoxythionaphthen. Warm sodium hydroxide solution converts the sulphoxide into thionaphthenquinone.

Bisoxythionaphthen is transformed by nitric acid (94%) in the presence of glacial acetic acid into the corresponding *sulphone*,



$C_6H_4<\genfrac{}{}{0pt}{}{CO}{SO_2}>C:C<\genfrac{}{}{0pt}{}{CO}{S}>C_6H_4$, m. p. above 300°. The *dibenzoyl* derivative, m. p. 228—229° (decomp.), and the *diacetyl* compound, m. p. 206°, of the corresponding dihydro product are described. The monosulphone is transformed by sodium hydroxide [illegible] into thionaphthenquinone and *thionaphthen-*

quinone-S-*dioxide*, $C_6H_4{<}\begin{smallmatrix}CO\\SO_2\end{smallmatrix}{>}CO$, m. p. 265°, which is reduced by zinc dust and glacial acetic acid to 3-hydroxy-1-dioxythionaphthen, m. p. 142° (cf. Lanfry, A., 1913, i, 193).

6 : 6′-Diethoxybisoxythionaphthen is converted in the usual manner into the *dibenzoyl* derivative, m. p. 260°, and the *diacetyl* derivative, m. p. 232° (decomp.), of the corresponding dihydro compound. H. W.

Angostura Alkaloids. II. Synthesis of Galipine. E. SPÄTH and H. EBERSTALLER (*Ber.*, 1924, **57**, [*B*], 1687—1690; cf. Späth and Brunner, this vol., i, 1226).—4-Methoxy-2-methylquinoline condenses with 3 : 4-dimethoxybenzaldehyde in the presence of zinc chloride at 105° to yield 4-*methoxy*-2-β-3′ : 4′-*dimethoxyphenylethinenylquinoline* [*hydrochloride*, m. p. 174—176° (decomp.)], which is reduced by hydrogen in the presence of palladised charcoal to 4-methoxy-2-β-3′ : 4′-dimethoxyphenylethylquinoline, $OMe{\cdot}C_9H_5N{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_3(OMe)_2$, m. p. 113·5° (*picrate*, m. p. 194°); the base is identical with natural galipine.

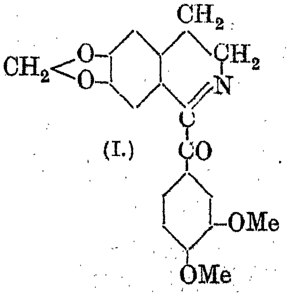
The isolation of the angostura alkaloids is conveniently effected by extraction of the bark with ethyl alcohol and concentration of the extract in a vacuum to a viscous syrup. The dark residue is treated with sodium hydroxide solution (25%), which dissolves the bulk of the coloured impurities and enables the alkaloids to be extracted with ether. The ethereal extract is repeatedly treated with dilute hydrochloric acid (1%), whereby cusparine and galipine are dissolved, whilst the more feebly basic alkaloids are removed from the remaining ethereal solution by hydrochloric acid (10%). Cusparine is separated from its mixture with galipine as the sparingly soluble oxalate. H. W.

Synthesis of ψ-Pelletierine. R. C. MENZIES and R. ROBINSON (*J. Chem. Soc.*, 1924, **125**, 2163—2168).—Aqueous solutions of calcium acetonedicarboxylate, glutardialdehyde, and methylamine were mixed and kept for 24 hours. The mixture was then acidified (to Congo-red) with hydrochloric acid, boiled to eliminate carbon dioxide, cooled, rendered alkaline, and the calcium removed as oxalate. Extraction with ether then gave an oil which was distilled in a high vacuum. The distillate afforded a sparingly-soluble *picrate*, which, after recrystallisation from water, decomposition with sodium hydroxide, and extraction with ether etc. afforded a crystalline base. Recrystallisation from light petroleum yielded crystals, m. p. 48·5°, identical with ψ-pelletierine. *Dipiperonylidene-ψ-pelletierine*, m. p. 226—227°, forms yellow, microscopic plates or prisms.

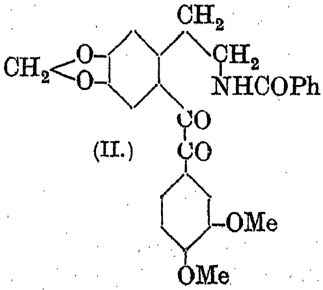
Adipdialdehyde similarly gave rise to an oily *base* possessing properties to be expected of a homo-ψ-pelletierine. It yielded a *dipiperonylidene* derivative and a *methiodide*. F. G. W.

Oxidation of Substituted 1-Benzyl-3 : 4-dihydro*iso*quinolines and a Synthesis of Papaveraldine. J. S. BUCK, R. D. HAWORTH, and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1924, **125**, 2176—2185).—When 6 : 7-methylenedioxy-3′ : 4′-dimethoxy-1-

benzyl-3 : 4-dihydro*iso*quinoline (cf. Haworth, Perkin, and Rankin, this vol., i, 1098) is exposed to the air in alcoholic solution, 3′ : 4′-*dimethoxy*-1-*benzoyl*-6 : 7-*methylenedioxy*-3 : 4-*dihydro*iso*quinoline* (I), m. p. 151° [*hydriodide*, m. p. 209—211°; *oxime*, m. p. 232° (decomp.)], is obtained. This, and its homologues, develop a brilliant green coloration when boiled with acetic anhydride. Reduction with tin and hydrochloric acid affords the corresponding 1 : 2 : 3 : 4-tetrahydro*iso*quinoline derivative (*loc. cit.*, 1099). Treatment with benzoyl chloride yields the *benzoyl* derivative (probably II; cf. Reissert, A., 1905, i, 925), pale yellow needles, m. p. 158°, from which (I) is re-formed on boiling with 40% sulphuric acid. When (I) is heated with methyl-alcoholic potassium hydroxide, it is oxidised to 3′ : 4′-*dimethoxy*-1-*benzoyl*-6 : 7-*methylenedioxy*iso*quinoline*, m. p. 208° [*picrate*, m. p. 206—207° (decomp.); *oxime*, m. p. 260° (decomp.)]. 3′ : 4′-*Methylenedioxy*-1-*benzoyl*-6 : 7-*dimethoxy*-3 : 4-*dihydro*iso*quinoline*, prisms, m. p. 151—152°, is obtained similarly to (I). The *hydriodide*, m. p. 192°; *picrate*, m. p. 227° (decomp.) after softening at 215°; and *oxime*, m. p. 223—224°, are described. It yields the tetrahydro*iso*quinoline derivative on reduction, and forms a pale yellow *benzoyl* derivative (see II), m. p. 151°, which yields an amorphous *monoxime*, and an o-*nitrobenzoyl* derivative, m. p. 175—176°. The action of aqueous permanganate, or of methyl-alcoholic potassium hydroxide, affords 3′ : 4′-*methylenedioxy*-1-*benzoyl*-6 : 7-*dimethoxy*iso*quinoline*, m. p. 199—200° [*picrate*, m. p. 243°; *oxime*, m. p. 263—264° (decomp.)], together with, in the latter case, a *substance*, $C_{19}H_{17}O_6N$, m. p. 294—296°. 6 : 7 : 3′ : 4′-*Tetramethoxy*-1-*benzyl*-3 : 4-*dihydro*iso*quinoline* was obtained as an oil (*picrate*, m. p. 168°) by the action of phosphoryl chloride in toluene on homoveratroylhomoveratrylamine. It was oxidised as above to 6 : 7 : 3′ : 4′-*tetramethoxy*-1-*benzoyl*-3 : 4-*dihydro*iso*quinoline*, a cream-coloured powder, m. p. 190—191°. The *hydrochloride*, $C_{20}H_{21}O_5N,HCl,H_2O$, yellow, m. p. 183°; *hydriodide*, orange, m. p. 186° (decomp.); *oxime*, m. p. 247—248° (decomp.); and *benzoyl* derivative, pale yellow, m. p. 160°, are described. When warmed with methyl-alcoholic potassium hydroxide, the base yielded 6 : 7 : 3′ : 4′-*tetramethoxy*-1-*benzoyl*iso*quinoline*, m. p. 208°, identical with papaveraldine.



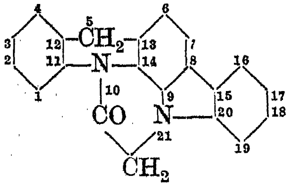
(I.)



(II.)

F. G. W.

Strychnine and Brucine. II. G. R. Clemo, W. H. Perkin, jun., and R. Robinson (*J. Chem. Soc.*, 1924, **125**, 1751—1804).—Perkin and Robinson (T., 1910, **97**, 305) have suggested that the strychnine molecule possessed the carbon–nitrogen skeleton of an anhydro-(5 : 10-dihydro)-acrindoline-21-acetic acid (annexed formula, the novel numbering of which should be noted). Substances having this skeleton have now been synthesised. The immediate aim of the work was to reproduce if possible either deoxystrychnine or dihydrostrychnoline (Tafel, A., 1892, 1012) but this has not been achieved.



When 9-amino-5 : 10-dihydroacridine (see below) is treated with ethyl chloroacetate and the product hydrolysed, *anhydro*-5 : 10-*dihydroacridine*-9-*aminoacetic acid*, m. p. 168° (a crystallographic description is given), is obtained [*acetyl* derivative, m. p. 174—175°; *nitroso* derivative, m. p. 167° (decomp.)]. When the nitroso derivative is reduced by zinc dust and acetic acid in presence of *cyclo*hexanone, condensation takes place and *anhydro*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*-21-*acetic acid*, yellow plates, m. p. 206°, is formed. This affords the corresponding *acid*, an amorphous substance, when treated with methyl-alcoholic potassium hydroxide, but the product is not wholly reconverted into the anhydride by the action of ethyl-alcoholic hydrochloric acid, some being also oxidised to *ethyl* 16 : 17 : 18 : 19-*tetrahydroacrindoline*-21-*acetate*, m. p. 172° (see below). Strychnic acid does not behave in a similar way. When the above anhydride is reduced electrolytically in alcoholic sulphuric acid suspension—and only by this means—it affords 21-β-*hydroxyethyl*-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline*, an amorphous, gummy substance which yields a crystalline *diacetyl* derivative, m. p. 235°. When the latter is hydrolysed by methyl-alcoholic potassium hydroxide it is presumably simultaneously oxidised as the product has the properties of an acridine derivative (fluorescent solution in sulphuric acid). In its formation and acetylation the parent substance resembles tetrahydrostrychnine (Tafel, *loc. cit.*), but not in this other behaviour.

Anhydrohexahydroacrindoline-21-acetic acid suffers partial reduction when it is distilled over zinc dust at 20 mm. and by repeated treatment is thus converted into 10 : 21-*etheno*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*, a yellow substance, m. p. 181—182°, which gives red salts (the *hydrochloride* and *sulphate* are described). This compound is formulated as an etheno compound, and not as an *N*-vinyl derivative, for reasons that are discussed in detail and are based on evidence published elsewhere (cf. this vol., i, 1345). As a by-product, formed by oxidation in the later operations, 16 : 17 : 18 : 19-*tetrahydroacrindoline*-21-*acetic acid*, an amorphous substance, is obtained; its *ethyl* ester forms orange prisms, m. p. 172°. From the etheno derivative, by reduction with sodium amalgam in presence of an excess of carbon dioxide, 10 : 21-*ethano*-

5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline*, yellow prisms, m. p. 209°, is produced; in this, as it yields no acetyl derivative, the 10 : 21 bridge is still intact. Further reduction, by electrolysis of an alcoholic sulphuric acid suspension at 35—45°, converts the ethano compound into what is most probably 21-*ethyl*-5 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*octahydroacrindoline*, m. p. 127° (yielding an *acetyl* derivative, m. p. 173°, and a *sulphate* which is decomposed by ammonia), together with 21-*ethyl*-5 : 6 : 7 : 8 : 9 : 10 : 15 : 16 : 17 : 18 : 19 : 20-*dodecahydroacrindoline*, a strongly basic resinous substance—the *sulphate*, m. p. 230° (decomp.), is not decomposed by ammonia—yielding an *acetyl* derivative, $C_{21}H_{27}N_2Ac$, which also is resinous. The ethenotetrahydro, ethano- and ethyl-octahydro, and the ethyldodecahydro compounds do not exhibit the physiological properties characteristic of strychnine.

Compounds having the complete "strychnine skeleton" were synthesised only in the above way; earlier abortive attempts resulted in the production of the following compounds, some of which, indeed, were made use of in the experiments described above.

2′-Nitrodiphenylamine-6-carboxylic acid, obtained from anthranilic acid and *o*-chloronitrobenzene, is converted by sulphuric acid at 100° into 9-nitroacridone (cf. Ullmann, A., 1907, i, 842), the 3(?)-*sulphonic acid* of which yields a *chloride*, m. p. 270—274°. When 9-nitroacridone is reduced with ammonium sulphide 9-aminoacridone is obtained, and this with ethyl bromoacetate affords (eventually) *acridone-9-aminoacetic acid*, a gelatinous substance; the *methyl* ester forms yellow prisms, m. p. 237—238°, and affords a *nitroso* derivative, decomp. 180°; the *ethyl* ester forms yellow needles, m. p. 195°, and affords a *nitroso* derivative, m. p. 185—186° (decomp.). The latter, the nitroso ethyl ester, undergoes a condensation when it is reduced with zinc and acetic acid in presence of *cyclo*hexanone, but in the reaction the carbethoxymethyl group is wholly removed, and the product is not the expected anhydroketohexahydroacrindolineacetic acid, but 5-*keto*-5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*, dull yellow prisms, m. p. above 380° (the *hydrochloride*, *hydrobromide*, *nitrate*, and *sulphate*, all bright red substances, are described). This substance is also obtained (and so its constitution verified) as follows: 9-aminoacridone is converted by the action of nitrous acid into *acridonediazole*, m. p. 266°, and this readily yields the desired product when it is reduced by zinc dust and acetic acid in presence of *cyclo*hexanone.

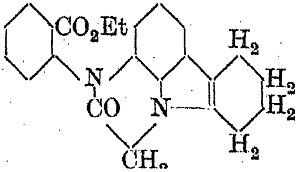
The above keto compound, when reduced by sodium amalgam and an excess of carbon dioxide, affords 5 : 10 : 16 : 17 : 18 : 19-*hexahydroacrindoline*, m. p. 187—205° (the *hydrochloride* and *sulphate* are red), which is oxidised by boiling its alcoholic solution in contact with air to 16 : 17 : 18 : 19-*tetrahydroacrindoline*, m. p. 230—231° (this also forms red salts: *hydrochloride*, *sulphate*, and *picrate*).

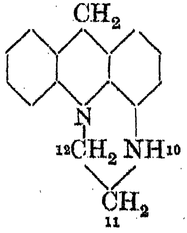
2′-*Aminodiphenylamine-6-carboxylic acid*, m. p. 210° (*hydrochloride*, m. p. 260°), is obtained by reducing the nitro compound mentioned above with ferrous sulphate and ammonia. This acid is converted at its m. p. into the *anhydro* derivative (2′-*aminophenylanthranil* ?), m. p. 250° [*acetyl* derivative, m. p. 248°; *nitroso* derivative, m. p. 202° (decomp.)]. The aminodiphenylaminecarboxylic acid interacts with phenanthraquinone to afford *flavinduline*-o-*carboxylic acid*, m. p. 310° (decomp.). It also yields, when treated with nitrous acid, 1-o-*carboxyphenyl*-1 : 2 : 3-*benztriazole*, m. p. 217° (decomp.); this product resisted all attempts to convert it into acridonediazole or into an indole derivative.

From *o*-phenylenediamine and *o*-chlorobenzoic acid, 6-*carboxydiphenylamine*-2′-o-*aminobenzoic acid* (s-*di*-o-*carboxyphenyl*-o-*phenylenediamine*), m. p. 258°, is obtained; this is decomposed, when heated under diminished pressure, and converted into s-*diphenyl*-o-*phenylenediamine*, m. p. 109°, b. p. 280—290°/40 mm., the *diacetyl* derivative of which has m. p. 281° [Wieland's base (A., 1913, i, 1386) is most probably *o*-aminotriphenylamine].

When 2′-aminodiphenylamine-6-carboxylic acid is treated with sodium formaldehyde-bisulphite followed by potassium cyanide and, finally, by sodium hydroxide, 6-*carboxydiphenylamine*-2′-*aminoacetic acid*, m. p. 212°, is produced; this, by the action of alcoholic hydrochloric acid, is converted into the ester of the anhydro derivative, namely, *anhydro*-6-*carbethoxydiphenylamine*-2′-*aminoacetic acid*, m. p. 153°, of which the *nitroso* derivative (m. p. 117°) undergoes the usual condensation when reduced in presence of *cyclo*hexanone, yielding *anhydro*-8-o-*carbethoxyphenylamino*-1 : 2 : 3 : 4-*tetrahydrocarbazole*-9-*acetic acid* (I), yellow prisms, m. p. 172°; the dibasic acid of which this is the anhydro ester, namely, 8-o-*carboxyphenylamino*-1 : 2 : 3 : 4-*tetrahydrocarbazole*-9-*acetic acid*, has m. p. 243° (*acetyl* derivative, m. p. 250°) and when it is heated with sulphuric acid gives no acrindoline derivative but only *anhydro*-8-o-*carboxyphenylamino*-1 : 2 : 3 : 4-*tetrahydrocarbazole*-9-*acetic acid*, m. p. about 255°.

(I.)





(II.)

9-*Amino*-5 : 10-*dihydroacridine*, m. p. 114°, is obtained either through 9-*nitrothioacridone*, m. p. 236° (from the nitroacridone and phosphorus pentasulphide), or, better, by reducing the nitroacridone itself with sodium amalgam in presence of an excess of carbon dioxide. Its *acetyl* derivative has m. p. 177°; when this is oxidised with potassium dichromate 9-*acetamidoacridine*, m. p. 117°, is obtained, and hydrolysis with boiling 60% sulphuric acid then affords 9-*aminoacridine*, orange prisms, m. p. 105—106° (*hydrochloride*, m. p. 234°, decomp.). The latter interacts with ethyl chloroacetate to afford *ethyl acridine*-9-*aminoacetate*, m. p. 109°

(the *acid* has m. p. about 185°, decomp.), the *nitroso* derivative (m. p. 115—117°) of which is remarkable in giving no condensation product when it is reduced with zinc and acetic acid in presence of *cyclo*hexanone.

The *toluene*-p-*sulphonyl* derivative, m. p. 169—170° (*hydrochloride*, m. p. 242°), of 9-aminoacridine interacts with ethyl toluene-*p*-sulphonate to yield the *toluene*-p-*sulphonyl* derivative (m. p. 175—176°) of 9-*ethylaminoacridine*, orange-red plates, m. p. 65° (*acetyl* derivative, m. p. 95°).

Anhydro-5 : 10-dihydroacridine-9-aminoacetic acid (see above) is converted by the action of phosphorus pentachloride into a *compound*, $C_{30}H_{23}O_3N_4ClP$, m. p. 175—178°.

When anhydrodihydroacridineaminoacetic acid is electrolytically reduced it yields what is probably 11 : 12-*dihydroacridoxaline* (II), a gummy substance with a pronounced irritant action on the skin. The *acetyl* derivative of this compound has m. p. 152°, but even when this is hydrolysed the parent reappears as a gum. It was thought at first that this product was the ethylaminoacridine described above (there being the two possibilities), but the independent preparation showed that this was not so.

The *toluene*-p-*sulphonyl* derivative (m. p. 190—191°) of 9-amino-5 : 10-dihydroacridine affords a β-*chloroethyl* derivative (m. p. 147—148°) when it is treated with β-chloroethyl toluene-*p*-sulphonate, but this resists condensation to form a dihydrocarboxaline ring. The analogous β-*hydroxyethyl* derivative (m. p. 154—155°) is obtained when ethylene chlorohydrin is used, and this also will not undergo intramolecular condensation. When it is oxidised in hot acetic acid solution with potassium dichromate, the *toluene*-p-*sulphonyl* derivative (m. p. 156°) of the corresponding acridine is obtained, and this affords the parent compound, namely, 9-β-*hydroxyethylaminoacridine*, m. p. 109—110°, when hydrolysed with boiling 60% sulphuric acid. This is reduced by treatment with sodium amalgam in presence of much carbon dioxide to 9-β-*hydroxyethylamino*-5 : 10-*dihydroacridine*, m. p. 122—123° (*diacetyl* derivative, m. p. 148°; partial hydrolysis affords the *monoacetyl* derivative, m. p. 147—148°); fruitless experiments were made to close the dihydrocarboxaline ring in this compound, using a variety of condensing agents.

When the potassium compound of the toluene-*p*-sulphonyl derivative of 9-amino-5 : 10-dihydroacridine and bromodimethylacetal are heated together at 100° in methyl-alcoholic solution the *dimethylacetalylsulphonyl* derivative, m. p. 121°, is obtained; subsequent treatment with ethyl-alcoholic hydrochloric acid produced an amorphous substance.

9-Amino-5 : 10-dihydroacridine and bromodimethylacetal (with sodium acetate, and a little copper, in alcoholic solution) afford eventually 9-*aminoacridine dimethylacetal*, m. p. 87°, which is converted by reduction with sodium amalgam into the corresponding derivative of the 5 : 10-dihydroacridine, m. p. 63—64°.

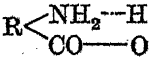
When the aminodihydroacridine interacts with ethyl bromoacetate, *ethyl anhydro*-5 : 10-*dihydroacridine*-9-*aminodiacetate*, m. p.

154—156°, is obtained, the parent *acid* of which has m. p. 192° (after losing 1 mol. MeOH—of crystallisation?). This acid decomposes when heated at 20 mm., yielding a distillate consisting of *anhydro*-5 : 10-*dihydroacridine* 9-*methylaminoacetic acid*, m. p. 131—132°.

6-*Nitro*-9-*methylacridone* (m. p. above 300°, prepared from 4-nitrotolylanthranilic acid) yields, when reduced with sodium amalgam in the manner indicated above, 6-*amino*-9-*methyl*-5 : 10-*dihydroacridine*, orange prisms, m. p. 118°, and 9-chloroacridone (Ullmann, *loc. cit.*) similarly affords 9-*chloro*-5 : 10-*dihydroacridine*, needles, m. p. 79° (unstable), or prisms, m. p. 90—91° (stable form).

W. A. S.

Determination of Constitution by Spectroscopic Methods. Constitution of Amino-acids. I. H. Ley and F. H. Zschacke (*Ber.*, 1924, **57**, [*B*], 1700—1707).—Comparison of the absorption curves of piperidinoacetic acid with those of its sodium salt, hydrochloride, ethyl ester, and sodium acetate shows that it is impossible that the acid exists in the normal form, $C_5H_{10}N\cdot CH_2\cdot CO_2H$, since the absorption of the acid is not intermediate between that of the sodium salt and the ester. The close identity of the absorption curves of the acid and sodium acetate suggests further that the normal form cannot be present to an appreciable extent. The choice between the constitutions indicated by the schemes



$R<\begin{matrix}NH_2\cdots H\\ CO\text{——}O\end{matrix}$ and $\cdot NH_3\cdot R\cdot CO_2'$ cannot be effected on the bases of optical measurements. In the case of aromatic amino-acids, such as *o*-aminobenzoic acid and the acids of the pyridine series, the neutral form greatly predominates.

H. W.

Stereochemistry of Saturated Tervalent Nitrogen. VI. Attempts to Prepare Optically Active Compounds of Tervalent Nitrogen.—(See i, 1299.)

6-Methoxy-1 : 2 : 3 : 4-tetrahydro*iso*quinoline. L. Helfer (*Helv. Chim. Acta*, 1924, **7**, 945—950).—The initial stages in the synthesis of this compound are described as follows: *m*-nitrobenzaldehyde ⟶ *m*-aminobenzaldehyde ⟶ *m*-hydroxybenzaldehyde ⟶ *m*-methoxybenzaldehyde ⟶ *m*-anisylacrylic acid ⟶ *m*-anisylpropionic acid ⟶ *methyl* m-*anisylpropionate* (m. p. 29—30°, b. p. 150—152°/14 mm.) ⟶ m-*anisylpropionamide* (m. p. 56°, b. p. 218—219°/9 mm.) $\rightleftharpoons$ β-m-*anisylethylamine* (b. p. 247—248° or 122—123°/7 mm.). The last substance is a strong base forming a *carbonate*; *hydrochloride*, m. p. 145—146°; *picrate*, m. p. 134°; and *chloroplatinate*, m. p. 204—205° (decomp.). The action of formaldehyde on β-*m*-anisylethylamine gives β-m-*anisylethylmethylene-amine*, a viscous oil. Evaporated to dryness with hydrochloric acid, this gives the *hydrochloride* of 6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*isoquin*oline*. The latter is a strong base (b. p. 143—144°/6 mm.), forming a crystalline *carbonate*; *hydrochloride*, m. p. 233—234°; *picrate*, m. p. 173—174° (decomp.); *chloroplatinate*, orange-red, m. p. 198°;

and *nitrosoamine*, a yellow oil. When the base is oxidised by alkaline permanganate, 4-methoxyphthalimide (m. p. 231°) is obtained together with some 4-methoxyphthalic acid (T., 1907, **91**, 103).
W. E. E.

Isatin and Related Compounds. VI. 5-Iodoisatin and 5 : 5′-Di-iodoindigotin. W. Borsche, H. Weussmann, and A. Fritzsche (*Ber.*, 1924, **57**, [*B*], 1770—1775).—5-*Iodoisatin*, m. p. 264—265°, is prepared by the action of iodine monochloride on a solution of isatin in glacial acetic acid or by the action of concentrated sulphuric acid on p-*iodo-oximinoacetanilide*, $C_6H_4I\cdot NH\cdot CO\cdot CH{:}N\cdot OH$, m. p. 180—182° (prepared from *p*-iodoaniline, hydroxylamine, and chloral hydrate). 5-*Iodoisatin*-3-*hydrazone*, decomp. 240° after becoming discoloured at 170°, is described. 5-*Iodo*-1-*methylisatin*, m. p. 175°, is obtained by methylation of 5-iodoisatin with methyl sulphate and sodium hydroxide, or from 1-methylisatin and iodine chloride. 5-Iodoisatin is transformed by acetone in the presence of aqueous-alcoholic potassium hydroxide solution into 6-*iodo*-2-*methylquinoline*-4-*carboxylic acid*, m. p. 290°, which passes at 300° into 6-*iodo*-2-*methylquinoline*, m. p. 107—108° (*picrate*, m. p. 194—195°). Similarly, acetophenone and 5-iodoisatin give 6-iodo-2-phenylquinoline-4-carboxylic acid, m. p. 249—250°, from which 6-*iodo*-2-*phenylquinoline*, m. p. 143—144°, is derived. 6-*Iodo*-2-*hydroxyquinoline*-4-*carboxylic acid*, m. p. above 320°, is converted by a solution of phosphorus pentachloride in phosphoryl chloride into a mixture of 2-*chloro*-6-*iodoquinoline*-4-*carboxylic acid*, m. p. 215—216°, and 6-*iodo*-2-*hydroxyquinoline*-4-*carboxylyl chloride*, m. p. 265—266°.

5-*Iodoisatin chloride*, m. p. 226—228°, prepared from iodoisatin and phosphorus pentachloride in the presence of benzene, is transformed by heating with aniline into 5-*iodo*-2-*aniloisatin*, m. p. 223—224°, and thence by the action of ammonium sulphide and hydrogen sulphide into 5 : 5′-*di-iodoindigotin*.

5-Iodoanthranilic acid, m. p. 212—214° (decomp.), is conveniently prepared by the action of iodine monochloride on anthranilic acid dissolved in glacial acetic acid. It is converted by acetic anhydride into 5-*iodo*-2-*acetamidobenzoic acid*, m. p. 241—242°. Attempts to prepare the latter compound by the direct iodination of acetamidobenzoic acid yielded a mixture of unchanged material and 3 : 5-*di-iodoanthranilic acid*, m. p. 232—233°; if a larger proportion of iodine chloride is used, 2 : 4 : 6-tri-iodoaniline, m. p. 186°, is also produced. 5-*Iodo*-2-*cyanomethylaminobenzoic acid*,

$$CN\cdot CH_2\cdot NH\cdot C_6H_3I\cdot CO_2H,$$

m. p. 217°, is obtained together with an unidentified *substance*, m. p. 184—186°, by the action of potassium cyanide and formaldehyde on 5-iodoanthranilic acid in aqueous solution. It is hydrolysed by 3*N*-sodium hydroxide solution to 5-*iodo*-2-*carboxymethylaminobenzoic acid*, m. p. 207—208°, which is more conveniently obtained from phenylglycine-*o*-carboxylic acid and iodine chloride. It appears to lose a part of the iodine when fused with potassium hydroxide.
H. W.

Transformation of Isatogen Derivatives into Isatins. P. Ruggli and W. Leonhardt (*Helv. Chim. Acta*, 1924, 7, 898—907).—The by-product previously obtained (this vol., i, 1106) from the action of acetic anhydride and sulphuric acid on 6-nitro-2-phenylisatogen varies according to the proportion of sulphuric acid. It is yellow (for additive products of nitrophenylisatogen and acetic anhydride, see below) for acid percentages below 3, and red when the percentage is 3 to 6, and then consists chiefly of 6-*nitro*-1-*phenylisatin*, m. p. 232° (*ammonium*, *potassium*, *barium*, and *silver* salts described; *methyl ether*, reddish-gold leaflets, m. p. 82°). The barium salt, when heated in acetic acid solution, affords 4-*nitro*-1-*phenylisatic acid*, yellow crystals, m. p. 288—290° (decomp.). With *o*-phenylenediamine, the nitrophenylisatin affords 6-*nitro*-1-*phenylindophenazine*, yellow needles, m. p. above 310° (decomp.). The *oxime* of the nitroisatin forms yellow needles, m. p. 227—230° (decomp.), and is converted by diazomethane into the *methyl ether*, golden-yellow tablets, decomp. 170—175°. The corresponding *hydrazone* forms yellow leaflets, m. p. 220—225° (decomp.), and the β-*phenylhydrazone*, brick-red needles, m. p. 238° (decomp.). The latter, when heated with excess of phenylhydrazine, gives 6-*amino*-1-*phenylisatin*-β-*phenylhydrazone*, red needles, m. p. 213° (*diacetyl* derivative, orange-yellow needles, m. p. 255—256°). From the above nitrophenylisatin mother-liquors, 4-*nitrobenzoylanthranil* (m. p. 179°) and 4-*nitrobenzoylanthranilic* acid (m. p. 252°) were also obtained. By treatment with acetic anhydride the latter is converted into the former.

Nitrophenylisatogen forms a labile *additive* compound (yellow needles, decomp. 65—70°) with acetic anhydride (1 mol.) when treated with a mixture of the latter with sulphuric acid. W. E. E.

Fission of the Pyridine Nucleus during Reduction. B. D. Shaw (*J. Chem. Soc.*, 1924, **125**, 1930—1934).—When pyridine is reduced with sodium and aqueous alcohol (95%) instead of absolute alcohol, little or no piperidine is formed, but ammonia is evolved and a resinous nitrogen-free product is obtained, with traces of a volatile oil, possibly pentamethylene oxide. Simple derivatives of pyridine also suffer this disruption (cf. Mumm and Brodersen, this vol., i, 82). Ammonia is readily given off when 2-stilbazole is similarly reduced and the product, after repeated treatment to ensure complete conversion, consists chiefly of 2-β-*phenylethyltetrahydropyran*, m. p. 77°. Quantitative experiments with pyridine indicate that the scission takes place at the dihydro stage of the reduction. W. A. S.

Vinyl Derivatives, especially of Carbazole and Tetrahydrocarbazole, and their Behaviour with Acids. G. R. Clemo and W. H. Perkin, jun. (*J. Chem. Soc.*, 1924, **125**, 1804—1814).—By interaction of toluene-*p*-sulphonanilide and β-chloroethyl toluene-*p*-sulphonate *toluene*-p-*sulphon*-β-*chloroethylanilide*, m. p. 76°, is obtained. When treated with potassium iodide in hot amyl alcohol, it affords the β-*iodo* analogue, m. p. 81—82°; with diethylamine in alcohol at 160° it yields a product from which, by hydrolysis, β-*diethylaminoethylaniline*, b. p. 163°/17 mm., is obtained; similarly, with *o*-chloroaniline, potassium carbonate and a little copper powder, the *toluene*-p-*sulphonyl* derivative, m. p. 110°, of β-o-*chlorophenylaminoethylaniline*, b. p. 238—242°/20 mm. (*hydrochloride*, m. p. 185°), is produced. Further, treatment with methyl-alcoholic potassium hydroxide effects the conversion into *toluene*-p-*sulphonvinylanilide*, m. p. 96—97°; this unites with bromine to form an unstable *dibromo* compound, which is converted by warm methyl-alcoholic potassium hydroxide into *toluene*-p-*sulphon*-β-*bromo*-α-*methoxyethylanilide*, m. p. 78—79°. The vinyl derivative is readily decomposed when it is treated with dilute sulphuric acid, the parent anilide and acetaldehyde being formed. This agrees, and so do the observations described below, with the results obtained by other investigators (cf. *e.g.*, von Braun and Kirschbaum, A., 1920, i, 154) of the behaviour of *N*-vinyl derivatives. β-Chloroethylaniline (cf. Nemirowsky, A., 1885, 741) is unstable; it "polymerises" to a chlorine-free solid substance of unknown constitution; its *hydrochloride*, m. p. 156—158°, is obtained by hydrolysing the above toluene-*p*-sulphonyl derivative with a mixture of acetic and hydrochloric acids. When part of the product is directly benzoylated (using a benzene solution of benzoyl chloride and an excess of sodium hydroxide), the chlorine atom is simultaneously removed and *benzo*-β-*hydroxyethylanilide*, m. p. 78°, is obtained. When β-chloroethylaniline hydrochloride is treated with sodium nitrite, it affords an oil which, by the action of alcoholic hydrogen chloride is converted into p-*nitroso*-β-*chloroethylaniline*, m. p. 90° (decomp. 120°), the *hydrochloride* of which has m. p. 182° (decomp.); when the intermediate oily nitrosoamine is reduced by zinc dust and acetic acid in presence of *cyclo*hexanone, β-*chloroethyltetrahydrocarbazole*, m. p. 56—57°, is obtained, together with a *by-product*, m. p. 141°. 9-*Vinyltetrahydrocarbazole*, b. p. 210°/24 mm., is produced by the customary treatment with methyl-alcoholic potassium hydroxide. When this is treated with 50% sulphuric or alcoholic hydrochloric acid it is decomposed and a solid product is formed; this is due apparently to interaction of the acetaldehyde and tetrahydrocarbazole produced, because if a little hydrazine be added to the reaction mixture, tetrahydrocarbazole is obtained. 9-Vinyltetrahydrocarbazole cannot be prepared from 9-β-*hydroxyethyltetrahydrocarbazole*, m. p. 69—70°, b. p. 230—235°/14 mm., which is obtained when β-hydroxyethylphenylnitrosoamine is reduced, as above, in presence of *cyclo*hexanone. Carbazole and β-chloroethyl toluene-*p*-sulphonate afford 9-β-*chloroethylcarbazole*, m. p. 130—131°, from which 9-*vinylcarbazole*, m. p. 66°, is readily obtained. This also is decomposed by acids, when hydrazine is present, and carbazole is regenerated; if the hydrazine be absent, a complex solid *substance* is produced.

W. A. S.

Reduction Products of 1-Nitro- and 3-Nitro-carbazole. [illegible] (*J. Amer. Chem. Soc.*, 1924, 46, 2326—2329).—[illegible] -nitrocarbazole, obtained by nitration of carbazole in acetic acid at 60° (cf. Ziersch, A., 1909, i, 961), on heating with alcoholic sodium or potassium hydroxide are reduced to 3-*azoxycarbazole*, yellow, m. p. 208—209°, and 1-*azoxycarbazole*, yellow, m. p. 183—185°, respectively, in yields of 70—80%. Reduction of the azoxycarbazoles in alcoholic solution with zinc dust gives an 80% yield of 3-*azocarbazole*, red, m. p. 215°, and 1-*azocarbazole*, reddish-brown, m. p. 196—197°, respectively. Reduction of 1-nitro-, 1-azoxy-, or 1-azo-carbazole with zinc dust in alcoholic potassium hydroxide yields 1-aminocarbazole, m. p. 226—228° (*acetyl* derivative, m. p. 170—171°). 3-Aminocarbazole, m. p. 254° (cf. Ruff and Stein, A., 1901, i, 619; Ullmann, A., 1898, i, 591) is similarly obtained from the corresponding 3-carbazole derivatives. R. B.

3-Hydroxyquinoline-4-carboxylic Acids. S. Berlingozzi and G. B. Capuano (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 91—94).—3-Hydroxy-2-methylquinoline-4-carboxylic acid (cf. this vol., i, 314) may be obtained by the condensation of isatoic acid with chloroacetone in presence of sodium hydroxide, and 3-hydroxy-2-phenylquinoline-4-carboxylic acid (*loc. cit.*) by the similar condensation of isatoic acid with ω-bromoacetophenone (cf. also A., 1923, i, 482).

3-*Hydroxy*-2-p-*anisylquinoline*-4-*carboxylic acid*, prepared similarly from isatoic acid and *p*-chloroacetylanisole, crystallises in lustrous, golden-yellow rosettes, m. p. about 190° (decomp.), and forms an intensely fluorescent alcoholic solution. When heated above its melting point, it loses carbon dioxide with formation of 3-hydroxy-2-*p*-anisylquinoline (cf. A., 1923, i, 483). The colours of various (precipitated) salts of the above acids are recorded.

T. H. P.

Structure of the Protein Molecule. E. Abderhalden and E. Schwab (*Z. physiol. Chem.*, 1924, **139**, 68—75).—By condensation of *iso*butylpiperazine (this vol., i, 876) with α-bromo*iso*hexoyl bromide, *di-α-bromo*iso*hexoyl*iso*butylpiperazine*, m. p. 283° (decomp.) after previously sintering, has been obtained. This reacts with ammonia to form *dileucyl*iso*butylpiperazine*, which, on reduction by the method previously employed (*loc. cit.*) yields a mixture of *iso*butylpiperazine and reduced dileucyl*iso*butylpiperazine (isolated as the *tetrahydrochloride*, $C_{20}H_{48}N_4Cl_4$). By similar methods of reduction, β-*amino-δ-methylpentan-α-ol* (*leucinol*), $CHMe_2·CH_2·CH(NH_2)·CH_2·OH$, isolated as the *hydrochloride*, has been obtained from leucylglycine, and 2-*methylpiperazine*, m. p. 245°, from glycyl-*d*-alanine anhydride. *Dichloroacetylmethylpiperazine* on treatment with ammonia gives *diglycylmethylpiperazine*. E. S.

Preparation of Compounds of Diketopiperazines with Amino-acids and Polypeptides. E. Abderhalden and E. Klarmann (*Z. physiol. Chem.*, 1924, **139**, 64—67).—When refluxed with chloroacetyl chloride for 2 hours at 60—70°, 2 : 5-dihydroxydihydropyrazine dibenzyl ether (Karrer, Gränacher, and Schlosser, this vol., i, 212) yields 1 : 4-di[chloroacetyl]-2 : 5-diketopiperazine

(A., 1923, i, 1025; this vol., i, 877), and not the expected *O*-dichloroacetyl derivative.

By heating glycine anhydride for 4 hours at 160° with thionyl chloride, a *substance*, $C_4H_2ON_2Cl_3$, m. p. 168—169° (uncorr.), is obtained. E. S.

Formation of Diketopiperazines from Polypeptides. E. Abderhalden and E. Komm (*Z. physiol. Chem.*, 1924, **139**, 147—168).—On heating in a sealed tube at 150—160° for 6 hours with water, dilute hydrochloric acid, or dilute sulphuric acid, dipeptides give the corresponding anhydrides (diketopiperazines) in a yield which may vary from 20—90% of the theoretical. The only exception to this statement so far encountered is *dl*-valyl-*dl*-leucine, which gave no anhydride under these conditions. Prolonged boiling of the dipeptides in aqueous solution gave only traces of anhydrides. Small amounts of anhydrides have been obtained similarly from some tripeptides, but in no case where the tripeptide was composed of more than two different amino-acids.

C. R. H.

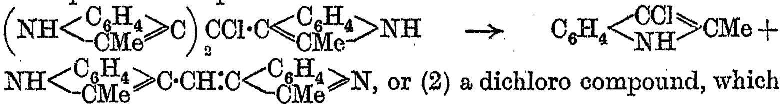
Parabanic Acid. R. Andreasch (*Monatsh.*, 1924, **45**, 9—12).—Thiocarbamide and cyanogen do not form thioparabanic acid. Interaction of acetylthiocarbamide and chloroacetic acid gave thiohydantoin. Attempts to add cyanogen to acetylthiocarbamide, and to carbamide and its methyl and phenyl derivatives were unsuccessful. Ethylparabanic acid has m. p. 127—128°.

The product of reduction of dimethylparabanic acid or cholestrophan (A., 1882, 1054) is definitely proved to be 5-hydroxy-1 : 3-dimethylhydantoin (cf. Biltz and Heidrich, A., 1921, i, 817), since it is shown that for its reoxidation to cholestrophan, dichromate equivalent to two hydrogen atoms per mol. is required.

F. M. H.

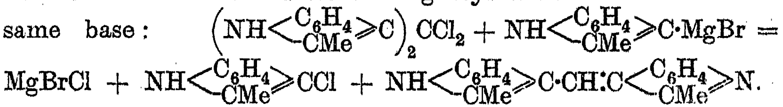
"Indigosol." A. Beil (*Z. angew. Chem.*, 1924, **37**, 745—746).—Leuco-indigotin is converted into an acid ester by treatment, in the presence of a tertiary base, with sulphur trioxide or substances which liberate it. The sodium salt of the ester, *Indigosol O*, is a nearly colourless powder, stable in the air and easily soluble in water, is unaffected by alkalis, and is decomposed by mineral acids only on prolonged boiling. Indigotin is regenerated by gentle oxidation (*e.g.*, with ferric chloride, or sodium nitrite, dichromate, or chlorates) in the presence of an acid. Indigosol has no affinity for vegetable fibres, but is substantive for wool, and possesses many practical advantages for the dyeing and printing of cotton and wool. [Cf. *B.*, 1924, 934.] W. T. K. B.

Indole Group. XI. Di-indylmethane. B. Oddo and G. Sanna (*Gazzetta*, 1924, **54**, 682—687).—An attempt to prepare an indole derivative corresponding with hexaphenylethane by treating magnesium indolyl (or 2-methylindolyl) bromide with carbon tetrachloride did not give the expected result, since, under the most varied conditions, this reaction yielded always the disubstituted methane derivative which is obtained from magnesium indolyl bromide and chloroform (A., 1922, i, 313; 1923, i, 715). Apparently attachment of more than two indole nuclei to one and the same carbon atom is not possible, probably owing to the proclivity of such nuclei to pass into the coloured indolidenic form. The reaction of magnesium 2-methylindolyl bromide with carbon tetrachloride may result in the initial formation of either (1) the normal trisubstituted leuco-derivative, which undergoes subsequent decomposition into the disubstituted coloured base:



$$\left(NH<\begin{smallmatrix}C_6H_4\\ CMe\end{smallmatrix}>C\right)_2CCl\cdot C<\begin{smallmatrix}C_6H_4\\ CMe\end{smallmatrix}>NH \longrightarrow C_6H_4<\begin{smallmatrix}CCl\\ NH\end{smallmatrix}>CMe + NH<\begin{smallmatrix}C_6H_4\\ CMe\end{smallmatrix}>C\cdot CH{:}C<\begin{smallmatrix}C_6H_4\\ CMe\end{smallmatrix}>N,$$

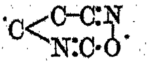
or (2) a dichloro compound, which then reacts with the excess of magnesyl derivative to form the same base:



$$\left(NH<\begin{smallmatrix}C_6H_4\\ CMe\end{smallmatrix}>C\right)_2CCl_2 + NH<\begin{smallmatrix}C_6H_4\\ CMe\end{smallmatrix}>C\cdot MgBr = MgBrCl + NH<\begin{smallmatrix}C_6H_4\\ CMe\end{smallmatrix}>CCl + NH<\begin{smallmatrix}C_6H_4\\ CMe\end{smallmatrix}>C\cdot CH{:}C<\begin{smallmatrix}C_6H_4\\ CMe\end{smallmatrix}>N.$$

T. H. P.

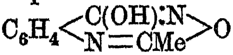
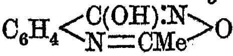
Isomeric Acylindazoles of K. von Auwers. J. Meisenheimer and A. Diedrich (*Ber.*, 1924, 57, [*B*], 1715—1723).—The general existence of 2-acylindazoles in isomeric labile and stable forms has been attributed by von Auwers and his co-workers (A., 1919, i, 455; 1920, i, 638, 640; 1922, i, 682, 684) to stereoisomerism conditioned by the presence of an asymmetric tervalent nitrogen atom. This conception is compatible with the tricyclic constitution of indazoles, but cannot be extended to the more recently adopted dicyclic constitution (cf. von Auwers, this vol., i, 878). The non-formation of stereoisomerides from 3-substituted indazoles suggests the possibility that one form of the "isomerides" is actually a 3-derivative, but this view is not supported by the experimental evidence now adduced. The only remaining alternative to the acceptance of the stereoisomeric formulation lies in the possibility that one form is a 1-compound. This conception has been rejected by von Auwers, since 1-acetylindazole, obtained from *o*-aminobenzaldoxime, is not identical with either of the "stereoisomeric 2-acetylindazoles." Re-examination of the former product renders very probable that it is not a derivative of indazole but is derived from the seven-membered ring,



$$C<\begin{smallmatrix}C-C{:}N\\ N{:}C\cdot O\end{smallmatrix}\Big].$$

The products described by von Auwers are therefore regarded as 1- and 2-acylindazoles.

3-*Benzoylindazole*, m. p. 188—189°, is prepared by the action of a considerable excess of magnesium phenyl bromide on 3-cyanoindazole in ethereal solution; the *acetyl* derivative, m. p. 121°, 2 : 4-*dinitrophenylhydrazone*, m. p. 277°, and the *oxime*, m. p. 175°, are described. 3-*Acetylindazole*, m. p. 182°, yields an *acetyl* derivative, m. p. 123°, an *oxime*, m. p. 222°, and a 2 : 4-*dinitrophenylhydrazone*, m. p. above 320°. The acyl compounds differ completely from von Auwers' "stereoisomeric" acetyl- and benzoyl-indazoles.

o-Aminobenzaldoxime is readily converted by glacial acetic acid and acetic anhydride into *o*-acetamidobenzaldoxime, which is transformed by concentrated sulphuric acid into "4 : 5-benzo-7-methylhept-1 : 2 : 6-oxdiazine"  $C_6H_4<\begin{matrix}C(OH):N\\N{=}CMe\end{matrix}>O$ (von Auwers' 1-acetylindazole). The substance is oxidised by perbenzoic acid in alcoholic solution to *3-hydroxy-4 : 5-benzo-7-methylhept-1 : 2 : 6-oxdiazine*,  $C_6H_4<\begin{matrix}C(OH):N\\N{=}CMe\end{matrix}>O$, m. p. 209°; attempts to establish the constitution of the compound by its production from the oxime of methyl acetylanthranilate were unsuccessful. *3-Acetoxy-4 : 5-benzo-7-methylhept-1 : 2 : 6-oxdiazine* has m.p. 117°. If von Auwers' conception is adopted the compound just mentioned must be identical with the diacetyl derivative of *o*-hydrazinobenzoic anhydride, m. p. 113—114°, and the oxidation product with *mono-acetyl-*o*-hydrazinobenzoic anhydride*, m. p. 211°; this, however, is not the case. The oxidised product may be regarded as a cyclic ether of benzhydroxamic acid; it could not be synthesised from *o*-aminobenzhydroxamic acid since the latter is immediately converted by acetic anhydride into the *diacetyl* derivative, m. p. 128°, with which, after hydrolysis, the desired ring closure could not be effected. H. W.

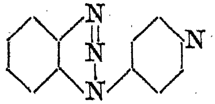
Constitution of Acylindazoles. K. von Auwers (*Ber.*, 1924, **57**, [*B*], 1723—1730).—As a result of the observations of Meisenheimer and Diedrich (preceding abstract) the constitution assigned previously to the "1-acylindazoles" is considered to have lost greatly in probability. The conception of these compounds as heptoxdiazines is not regarded as established, since the constitution of 3-hydroxy-7-methyl-4 : 5-benzohept-1 : 2 : 6-oxdiazine has not been placed beyond doubt and proof has not been adduced that the oxidation takes place without rupture of the ring of the parent compound.

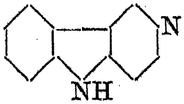
The "1-acylindazoles" are conveniently prepared by dissolving *o*-aminobenzaldoxime in the requisite acid and saturating the solution with dry hydrogen chloride at the atmospheric temperature or by treating a solution of the acylated oxime in glacial acetic acid in the same manner. "1-Acetylindazole" is converted by methyl iodide into an amorphous *methiodide*, $C_{10}H_{11}ON_2I$, decomp. above 90°, by bromine in glacial acetic acid into a very unstable *dibromide* and by the halogen in dilute hydrochloric acid solution into a *monobromo* derivative, m. p. 168—169°. 1-iso*Butyrylindazole* (or 7-iso*propyl-4 : 5-benzohept-1 : 2 : 6-oxdiazine*) has m. p. 108—108·5°; the *nitrate* and the additive *compound* with mercuric chloride dissolve sparingly in water. 1-iso*Valerylindazole* (7-iso*butyl-4 : 5-benzohept-1 : 2 : 6-oxdiazine*) has m. p. 85—86°, $d_4^{20·7}$ 1·0620, $n_\alpha^{20·4}$ 1·58638; the *nitrate* and the additive *compound* with mercuric chloride have been prepared. 1-*Benzoylindazole* (7-*phenyl-4 : 5-benzohept-1 : 2 : 6-oxdiazine*), m. p. 141° (the *nitrate* and the additive *compound* with mercuric chloride are described), [illegible] from *o-benzamidobenzaldoxime*, m. p. 163—164°. [illegible] propionic acid, propionic anhydride, and hydrogen chloride yield 1-*propionyl-3-methylindazole* (3-*methyl-7-ethyl*-4 : 5-*benzohept*-1 : 2 : 6-*oxdiazine*), m. p. 138°, which gives a *nitrate* and an additive *compound* with mercuric chloride. 1-Formyl-3-phenylindazole (3-phenyl-4 : 5-benzohept-1 : 2 : 6-oxdiazine), m. p. 167—168°, gives an additive *compound* with mercuric chloride. 1-*Benzoyl-3-phenylindazole* (3 : 7-*diphenyl*-4 : 5-*benzohept*-1 : 2 : 6-*oxdiazine*), m. p. 168—169°, and its additive *compound* with mercuric chloride are described.

Benzaldehyde and *o*-aminobenzaldoxime yield the *compound* $C_{14}H_{14}O_2N_2$, m. p. 135—136°, which gives a *monobenzoyl* derivative, m. p. 138—139°. The *benzoyl* derivative of *o*-nitrobenzaldoxime has m. p. 120—121°. H. W.

5-Carboline and some Derivatives. R. ROBINSON and S. THORNLEY (*J. Chem. Soc.*, 1924, **125**, 2169—2176).—N-γ-*Pyridyl-o-phenylenediamine*, m. p. 173·5°, obtained by heating 4-chloropyridine (b. p. 41°/13 mm.; 49°/18 mm.) with *o*-phenylenediamine at 98—140°/40 mm., forms a *hydrochloride*, and yields a *base*, probably γ-pyridylbenziminazole, m. p. 123°, when boiled in absolute formic acid. 1-γ-*Pyridylbenzotriazole* (I), m. p. 113·5° [*trihydrate*, m. p. 82°; *hydrochloride*, m. p. 262° (decomp.)], obtained from the above pyridyl-*o*-phenylenediamine by the action of nitrous acid, yields 5-*carboline* (II), m. p. 225°, when heated with excess of phosphoric acid (*d* 1·75). 5-Carboline distils unchanged at atmospheric pressure. The *hydrogen oxalate*, m. p. 226° (decomp.), and the *picrate* are described. The *methosulphate* when treated with hot concentrated potassium hydroxide yields 5-*methyl*-5-*isocarboline* (III), m. p. 203—204°, subliming at 138° in a vacuum. This base is hygroscopic and its aqueous solution is strongly alkaline. The *methosulphate*, m. p. 210—211°, with potassium hydroxide gives a colourless precipitate. 5-Carboline is reduced by sodium and *n*-butyl alcohol to 3 : 4 : 5 : 6-*tetrahydro-5-carboline* (IV), m. p. 215·5°, a strong base; 5-*acetyl* derivative, m. p. after softening, 254·5°. *Acetyltriacetonaminephenylhydrazone*, m. p. 107°, could not be transformed into an indole derivative, and therefore possibly has the structure (V). When triacetonamine-methylphenylhydrazone is warmed with dilute sulphuric acid, 1 : 4 : 4 : 6 : 6-*pentamethyl*-3 : 4 : 5 : 6-*tetrahydro-5-carboline* is obtained. This (+1 MeOH) has m. p. 80—86° after softening at 78°. After being heated at 111°, the substance resolidifies, and has m. p. 92—93°. Crystallised from

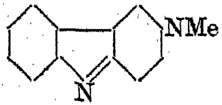
(I.)

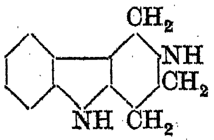




(II.)

(III.)





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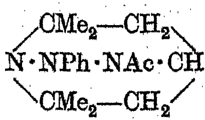


(V.)

light petroleum, it has m. p. 180° after sintering at 160°, and partly melting and resolidifying at 170°. F. G. W.

Effect of Sulphur on the Colour of Triphenylmethane Dyes. H. S. Holt and E. E. Reid (*J. Amer. Chem. Soc.*, 1924, **46**, 2329—2333).—The auxochromic effect of the alkylthiol group in triphenylcarbinol derivatives observed by Brand and Stallmann (A., 1921, i, 664) has now been observed in a series of malachite-green derivatives containing the alkylthiol group in the ortho or para position in the third ring. The auxochromic effect is greatest when the sulphur occupies the para position, but diminishes with increasing mass of the alkyl group. The methylthiol group is a stronger auxochrome than methoxyl, and the shift is towards the blue.

p-Aminophenyl methyl sulphide, obtained by the methods previously described (Waldron and Reid, this vol., i, 95; Foster and Reid, this vol., i, 1243), when diazotised and treated with cuprous bromide and potassium bromide, yields p-*bromophenyl methyl sulphide*, m. p. 27°. p-*Bromophenyl* iso*propyl sulphide*, b. p. 120°/11 mm., d_{25}^{25} 1·2338; p-*bromophenyl* iso*amyl sulphide*, b. p. 140—143°/15 mm., d_{25}^{25} 1·1467; p-*bromophenyl benzyl sulphide*, m. p. 48°; p-*bromophenyl methyl sulphone*, yellow, m. p. 97·5°; o-*bromophenyl* iso*propyl sulphide*, b. p. 130—135°/11 mm., d_{25}^{25} 1·2804, and o-*bromophenyl phenyl sulphide*, b. p. 175—177°/12 mm., d_{25}^{25} 1·3733, were similarly prepared. With the exception of *p*-bromophenyl benzyl sulphide and methyl sulphone and *o*-bromophenyl phenyl sulphide, which do not react, these bromophenyl alkyl sulphides were convertible in presence of iodine into Grignard reagents; the latter when treated with Michler's ketone in benzene solution yielded the dyes $(NMe_2{\cdot}C_6H_4)_2C(OH){\cdot}C_6H_4{\cdot}SR$ as orange solids turning green on exposure to air. R. B.

Constitution of Guinea-green B. H. Wales (*J. Amer. Chem. Soc.*, 1924, **46**, 2124—2128).—Guinea-green B is sodium hydrogen *s*-*pp*′-dibenzyldiethyldiaminotriphenylcarbinoldisulphonate. The free acid is brown and the disodium salt colourless, and the "organic material not dye" present in Guinea-green B is mainly the disodium salt. The free acid titrates very slowly with titanous chloride, and the higher results frequently obtained by very slow titration are due to the slow conversion of the disodium salt into the more readily reducible sodium hydrogen salt. The latter can be titrated in the presence of the disodium salt by titrating at 60—70° in the presence of sodium hydrogen tartrate. The titration can be checked by a spectrophotometric method, using a disodium phosphate–acetic acid buffer solution, p_{H} 6·0. R. B.

Reduction of certain Vat Dyes by means of Alkaline Sodium Hyposulphite. J. H. Yoe (*J. Physical Chem.*, 1924, **28**, 1211—1217).—The rate of reduction of ponsol-blue G (chloroanthraquinone-1 : 2 : 1′ : 2′-dihydroazine) by alkaline sodium hyposulphite at 40° is very great, the consequent peptisation, however, is less rapid; similar to ponsol-yellow G (A., 1923, i, 236).

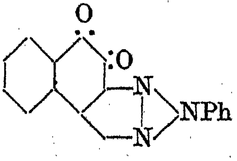
The reduced dye is in colloidal solution and is coagulated by salts. The amount of dye peptised was determined by the change in colour of the solution with time, and shows that the hyposulphite concentration has no effect above a certain value and that the optimum conditions are obtained with $0{\cdot}25N$-sodium hydroxide.

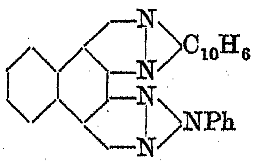
M. B. D.

o-Quinones derived from 2-Aryl-αβ-naphthatriazoles. G. Charrier (*Gazzetta*, 1924, **54**, 610—616).—Treatment of certain 2-aryl-αβ-naphthatriazoles with potassium dichromate and sulphuric acid under conditions which convert phenanthrene into phenanthraquinone results in the quantitative formation of the corresponding quinones. That the latter are ortho-quinones of the phenanthraquinone type is shown by their marked physical and chemical resemblance to phenanthraquinone and by their reaction with o-diamines to give the corresponding azines and with phenylhydrazine hydrochloride to form the hydroxyazo derivatives. It seems probable that anthracene bears the same relation to the ββ-naphthatriazoles that phenanthrene does to the αβ-naphthatriazoles.

2-*Phenyl-αβ-naphthatriazolequinone* (I), obtained by oxidation of 2-phenyl-αβ-naphthatriazole, forms orange-yellow needles, m. p. 207°, sublimes unchanged, and with hot alcoholic potassium hydroxide yields the brownish-green coloration characteristic for o-quinones. Its *benzeneazohydroxy* derivative,

(I.)





(II.)

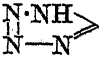
$$NPh{:}N{\cdot}C_{10}H_4N_3Ph{\cdot}OH,$$

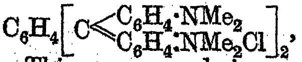
bright red needles, m. p. 232°, is obtained by the action of phenylhydrazine. The corresponding *naphthazine* (II), forms a microcrystalline, yellow powder, m. p. 262°, and yields deep red salts.

2-p-*Chlorophenyl-αβ-naphthatriazolequinone*, $C_{16}H_8O_2N_3Cl$, forms golden-yellow needles, m. p. 204°, its *benzeneazohydroxy* derivative, orange needles, m. p. 227°; the corresponding *naphthazine* is a yellow powder, m. p. 280°.

T. H. P.

Hydrolysis of Auramine. W. C. Holmes and J. F. Darling (*J. Amer. Chem. Soc.*, 1924, **46**, 2343—2348).—The hydrolysis of auramine in aqueous solution has been studied using a volumetric method based on the titration of the dye with a standard indigotin solution. The velocity of hydrolysis increases with the temperature and with the acidity of the solution, and, as in the hydrolysis of sucrose and of esters, the catalytic activity of the hydrogen ions is stimulated by the presence of other ions. The rate of hydrolysis is not influenced to a measurable extent by the relative purity of the dye samples used, and hydrolysis with dilute hydrochloric acid affords a convenient volumetric method for the determination of auramine or auramine-G. At the end of the hydrolysis, the solution is made alkaline and the ammonia distilled over and titrated, the small amount of dye unhydrolysed by the acid being decomposed by the alkali into Michler's ketone and ammonia. Auramine-G is less readily hydrolysed than auramine. R. B.

Action of Azoimide on Azodicarboxylic Esters. R. STOLLÉ and G. ADAM (*Ber.*, 1924, **57**, [*B*], 1656—1659).—Azoimide and methyl azodicarboxylate in the presence of ethyl or amyl ether give 5-*methoxytetrazole*,  $\begin{matrix}N\cdot NH\\ \|\quad\ \ \\ N-N\end{matrix}\!\!>C\cdot OMe$, m. p. 159° (decomp.), and methyl iminodicarboxylate, $NH(CO_2Me)_2$, m. p. 134°. Under similar conditions, ethyl azodicarboxylate gives 5-hydroxytetrazole, 5-*ethoxytetrazole*, m. p. 98° (the *silver* salt is described), and ethyl iminodicarboxylate, m. p. 48°. The alkoxytetrazoles are readily hydrolysed by 20% hydrochloric acid to 5-hydroxytetrazole, m. p. 254° (decomp.). H. W.

Synthesis of Terephthal-green and Terephthal-brilliant-green from Cymene. M. T. BOGERT and P. S. NISSON (*Proc. Nat. Acad. Sci.*, 1924, **10**, 421—426).—Terephthalyl chloride, prepared from cymene through methyl terephthalate (cf. Bogert and Harris, A., 1920, i, 65), interacts with dimethylaniline at 100° in presence of zinc chloride or other condensing agent, yielding the *dye*  $C_6H_4\left[C<\begin{matrix}C_6H_4\cdot NMe_2\\ C_6H_4{:}NMe_2Cl\end{matrix}\right]_2$, eventually isolated as zinc double salt. This compound is analogous to malachite-green and is termed by the authors "terephthal-green." The analogue of brilliant-green, termed "terephthal-brilliant-green" is obtained when diethylaniline is used. The two dyes both give yellower shades of green (on silk or wool) than their prototypes; they are more fugitive to light but faster than the latter to washing, milling, perspiration, and stoving, and are equally resistant to acid, alkali, or a bleaching solution. When terephthalyl chloride and dimethylaniline are brought together without a condensing agent, interaction takes place, not at 100°, but when the mixture is boiled; methyl chloride is evolved, and the *methylanilide*, $C_6H_4(CO\cdot NMePh)_2$, m. p. 212—213°, is formed (cf. the action of benzoyl chloride on dimethylaniline, Hess, A., 1885, 783). W. A. S.

Behaviour of Acetylene towards Nitrogen. L. FRANCESCONI and A. CIUSLO (*Gazzetta*, 1924, **54**, 687—697).—Under the influence of the silent electric discharge, a mixture of acetylene and nitrogen yields a compound which contains nitrogen and has a fulvene structure, and may be termed *pernitrogenated azofulvene*. This compound forms reddish-yellow laminæ, has a strong aromatic odour, and decomposes violently, without melting, at above 210°. When heated in a closed tube with solid potassium hydroxide, a basic odour recalling that of nicotine is emitted. Like the similar substances described by Losanitsch (A., 1908, i, 866; ii, 32), the [illegible] increases rapidly in weight in the air, giving a darker, [illegible] *azofulvene* which decomposes violently at 230—

235° and effects active discharge of an electrometer. It absorbs chlorine, bromine, and iodine in considerable quantities and reacts with other substances. T. H. P.

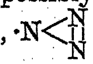
Electrometric Studies on Azo and Hydrazo Compounds. E. BILLMANN and J. H. BLOM (*J. Chem. Soc.*, 1924, **125**, 1719—1731).—An investigation of the reduction potential of the system azo compound–hydrazo compound on the same lines as those with quinhydrone and alloxantin for subjects (cf. A., 1923, ii, 605; 1921, ii, 372).

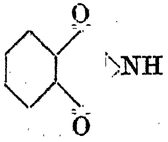
Two pairs of compounds were studied, *viz.*, 3 : 3′-diaminoazobenzene (termed azoaniline) and the corresponding hydrazo compound, and 3 : 3′-diamino-4 : 4′-dimethylazobenzene (termed azotoluidine) and the corresponding hydrazo compound. These were chosen because, being basic in character, they could be readily dissolved in acid to solutions of suitable concentration. At a temperature of 291° Abs. and a hydrogen pressure of 760 mm. the reduction potential for the azo–hydrazoaniline system (in 0·1*N*-hydrochloric acid) is 0·4137 volt, and for the azo–hydrazotoluidine system 0·3754 volt. The potential of the azo–hydrazo electrode, depending as it does on the proportion of azo to hydrazo compound, changes with time; this is evidently due to the conversion of the hydrazo compound into a benzidine or semidine derivative. From the observations made, the velocity constant of this conversion has been calculated for the two examples studied. W. A. S.

Preparation of Thio or Seleno Derivatives of Primary Aromatic Amines. FARBWERKE VORM. MEISTER, LUCIUS, UND BRÜNING (D.R.-P. 386615; from *Chem. Zentr.*, 1924, i, 2631).—Derivatives of the hypothetical thiohydroxylamine, $NH_2{\cdot}SH$, or dialkyldithiohydroxylamines, $RN(SR')_2$, are obtained by treating the condensation products of aromatic amines and aldehydesulphoxylates with hydrogen sulphide, mercaptans, etc., or hydrogen selenide, preferably in faintly acid solution :

$$R{\cdot}NH{\cdot}CH_2{\cdot}O{\cdot}SOH+R'{\cdot}SH=R{\cdot}NH{\cdot}SR'+CH_2O+S+H_2O.$$

The products separate as yellow precipitates; the following are described : *product* from hydrogen sulphide and *o*-toluidine *N*-methylenesulphoxylate, m. p. about 97°; the crystalline *product* from *p*-aminobenzoic acid and sodium formaldehydesulphoxylate, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}OSONa,2H_2O$, reacts with thioacetic acid to give S-*acetyl*-p-*thiohydroxylaminobenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}SAc$, m. p. 153°. Anthranilidomethylenesulphoxylate and ethyl mercaptan afford p-*ethylthiohydroxylaminobenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}SEt$, m. p. 97—99°. Aniline *N*-methylenesulphoxylate and thioacetic acid yield *SS*-diacetyldithiodihydroxyaniline, $NPh(SAc)_2$, m. p. 72°. Anthranilidomethylenesulphoxylate reacts with hydrogen selenide at 40—50° to give a *substance*, $C_{16}H_{14}O_6N_2SSe$, m. p. 40°, decomp. 80°. The condensation *product* of *o*-phenylenediamine and formaldehydesulphoxylate reacts with hydrogen selenide to give a *substance*, $C_{14}H_{19}O_7N_4S_3Se$, reddish crystals, m. p. 183—184°. F. A. M.

Derivatives of Azoimide. A. KORCZYŃSKI [with ST. NAMYSLOVKI] (*Bull. Soc. chim.*, 1924, [iv], **35**, 1186—1194).—The replacement of halogen atoms by azide groups when substituted quinones are treated with azoimide (Fries and Ochwat, A., 1923, i, 842) is a general reaction and mobile halogen atoms in compounds such as picryl chloride are replaced in the same way. With the unsubstituted naphthaquinones, azoimide reacts with the CH group ortho to the carbonyl yielding products, $C_{10}H_5O_2N$, which are analogous to the anthranils obtained by Schaarschmidt (A., 1916, i, 856) and by Gattermann (A., 1916, i, 857; 1921, i, 818). The diazido-α-naphthaquinone obtained by Fries and Ochwat (*loc. cit.*) could not be transformed into a dianthranil, and to account for the resistance of the benzene ring in the naphthalene molecule to the formation of a dianthranil, the annexed formula is suggested for the mono-anil. This finds some support in the behaviour of sulphuryl azide towards *p*-xylene (Curtius and Schmidt, A., 1922, i, 776). The azides are slightly stable, and although the azide group exercises an important influence on the colour of these compounds, this influence is irregular, and the azide group sometimes functions as a bathochrome and sometimes as hypsochrome, possibly in consequence of a change of structure in the group N_3,  $\cdot N{<}\begin{matrix}N\\ |\\ N\end{matrix} \rightleftharpoons \cdot N{:}N{:}N$. The statement that azides on alkaline reduction yield hydrazo compounds could not be confirmed.



On treatment with one equivalent of sodium azide in glacial acetic acid at 100°, chloroanil is converted into 3 : 5 : 6-*trichloro-2-azido*-p-*benzoquinone*, dark orange needles, m. p. 147—149°, exploding slightly on rapid heating, whilst with two equivalents of azide in boiling alcoholic solution 3 : 6-dichloro-2 : 5-diazido-*p*-benzoquinone is obtained, a slight excess of sodium azide giving a small quantity of reddish-violet explosive *substance*, probably the triazidochloroquinone. Excess of sodium azide in alcoholic solution at 20° converts the trichloroazidoquinone into tetrazido-*p*-benzoquinone. Similarly, tetrabromo-*o*-benzoquinone in glacial acetic acid yields an explosive, black substance which is probably *tetra-azido*-o-*benzoquinone*. Tetrabromodiphenoquinone in alcoholic suspension yields tetra-azidodiphenoquinone, a black powder which explodes at 30° or by friction or shock. 1 : 4-Naphthaquinone in acetic acid with one equivalent of sodium azide yields 2 : 3-*imino*-1 : 4-*naphthaquinone*, reddish-brown laminæ, m. p. 203—204°, also crystallising with 1 mol. of acetic acid (lost at 110°). Similarly, 1 : 2-naphthaquinone yields 3 : 4-*imino*-1 : 2-*naphthaquinone*, brown laminæ, losing acetic acid of crystallisation at 110°, then decomp. 300°. 2-Aminofluorenone, obtained by reduction of 2-nitrofluorenone with sodium sulphide, on diazotisation and treatment of the diazonium chloride with sodium azide, gives 2-azidofluorenone, yellow laminæ, darkening at 115°, m. p. 117°, slightly explosive. On heating in an atmosphere of carbon dioxide, boiling in glacial acetic acid, or exposing to light, the azide is converted into a [illegible] amorphous *substance*, $C_{13}H_7ON$, not melting below 300°.

Similarly, aminoazobenzene is converted into p-*azidoazobenzene*, pale yellow needles, m. p. 91—93°, and toluylene-red, obtained by boiling *p*-nitrosodimethylaniline with *m*-tolylenediamine and treatment with ammonia to precipitate the colour but leave the hydro-base in solution, gives 3-*azido*-6-*dimethylamino*-2-*methylphenazine*, red needles, m. p. 171—172° (decomp.).

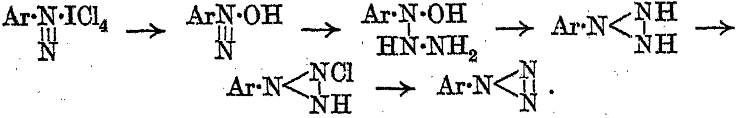
Picryl chloride in alcoholic solution reacts with aqueous sodium azide giving 2 : 4 : 6-trinitro-1-azidobenzene, m. p. 89—90° (decomp.), which darkens in colour on exposure to light and on boiling with acetic acid is converted into 4 : 6-*dinitro*-1 : 2-*dinitrosobenzene*, pale yellow needles, m. p. 172°, decomposed by light, which is also obtained directly from picryl chloride by the action of sodium azide in acetic acid solution at 100°. On warming with aniline in ethereal solution, picryl azide is converted into 2 : 4 : 6-trinitrodiphenylamine (Bamberger and Müller, A., 1900, i, 217). R. B.

Diazonium Tetrachloroiodides and Chloroplumbates. F. D. Chattaway, F. L. Garton, and G. D. Parkes (*J. Chem. Soc.*, 1924, **125**, 1980—1991).—Diazonium tetrachloroiodides, $Ar{\cdot}N_2(Cl_4I)$ (cf. Chattaway and Garton, this vol., i, 270), are obtained, in quantitative yield, when cooled solutions of diazonium chlorides are poured into cooled solutions of iodine trichloride in strong hydrochloric acid. They can be preserved indefinitely in sealed tubes or in an atmosphere of dry chlorine, and react generally in the same way as simple diazonium salts. With hydriodic acid, iodine is liberated quantitatively: $Ar{\cdot}N_2{\cdot}ICl_4+4HI=ArI+N_2+2I_2+4HCl$, this rendering iodometric analysis possible. When warmed with cuprous chloride or bromide in concentrated acid solution, or with potassium cyanocuprite, the diazonium tetrachloroiodides yield chloro, bromo, or cyano compounds, always accompanied by small quantities of the iodo derivative. The action of water yields phenols, with chlorophenols as by-products, whilst the action of alcohol causes the replacement of the diazo group chiefly by chlorine, and only to a lesser extent by hydrogen. The following *diazonium tetrachloroiodides*, yellow, crystalline powders, melting with decomposition at the temperatures quoted, are described: o-*toluene*-, 81·5°; p-*toluene*-, 95°; o-*chlorobenzene*-, 148°; p-*chlorobenzene*-, 111°; 2 : 4-*dichlorobenzene*-, 150°; 2 : 5-*dichlorobenzene*-, 141°; 2 : 4-*dibromobenzene*-, 120°; 2 : 4 : 6-*tribromobenzene*-, 135°; o-*nitrobenzene*, 125·5°; m-*nitrobenzene*-, 92°; and p-*nitrobenzene*-, 103°.

Diazonium chloroplumbates, $(Ar{\cdot}N_2)_2(PbCl_6)$, are obtained by the addition of solutions of diazonium salts to solutions of lead tetrachloride in strong hydrochloric acid. They form insoluble, yellow, crystalline solids, stable in the dry state, exploding at definite temperatures which vary only slightly according to the rate of heating. Their reactions are similar to those of the diazonium tetrachloroiodides, except for the absence of iodine. The following *diazonium chloroplumbates*, exploding at the temperatures stated, are described: o-*toluene*-, 78—80°; 2 : 4-*dichlorobenzene*-, 183—184°; p-*bromobenzene*-, 139—141°; 2 : 4-*dibromobenzene*-, 117—118°;

2 : 4 : 6-*tribromobenzene-*, 114—116°; o-*nitrobenzene-*, 120—122°. The following diazonium chloroplumbates previously described (Sakellarios, this vol., i, 220) explode at the following temperatures: benzene-, 80—81°; *p*-chlorobenzene-, 145—150°; *p*-toluene-, 72—75°; *m*-nitrobenzene-, 161—163°; and *p*-nitrobenzene-, 132—133°.

When diazonium tetrachloroiodides or chloroplumbates are added to concentrated aqueous ammonia, azoimides are obtained in good yields, probably according to the scheme:

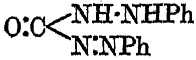


$$\mathrm{Ar{\cdot}\overset{\displaystyle N{\cdot}ICl_4}{\underset{\displaystyle N}{|||}}} \rightarrow \mathrm{Ar\overset{\displaystyle N{\cdot}OH}{\underset{\displaystyle N}{|||}}} \rightarrow \mathrm{Ar{\cdot}N{\cdot}OH \atop HN{\cdot}NH_2} \rightarrow \mathrm{Ar{\cdot}N{<}{NH \atop NH}} \rightarrow \mathrm{Ar{\cdot}N{<}{NCl \atop NH}} \rightarrow \mathrm{Ar{\cdot}N{<}{N \atop N}}.$$

2 : 5-*Dichlorophenylazoimide*, pale yellow crystals, m. p. 30°, and o-*tolyl azoimide*, pale yellow oil, b. p. 70°/20 mm., are described.

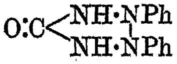
1-(2 : 4-*Dichlorophenyl*)-1 : 2 : 3-*triazole*, obtained by the action of 2 : 4-dichlorophenylazoimide on acetylene in acetone solution at 100° under pressure (cf. Dimroth, A., 1910, i, 645), has m. p. 80°. 1-(2 : 5-*Dichlorophenyl*)-1 : 2 : 3-*triazole*, m. p. 78°; 1-(2 : 4-*dibromophenyl*)-1 : 2 : 3-*triazole*; 1-o-*tolyl*-1 : 2 : 3-*triazole*, yellow oil; and 1 : 1′-(4 : 4′-*diphenylyl*)*bis*-1 : 2 : 3-*triazole*, pale yellow needles, m. p. 326° (decomp.), were prepared. *o*-Tolyl azoimide reacts with ethyl acetoacetate in presence of sodium ethoxide to form 1-o-*tolyl*-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*, m. p. 138° (decomp.), whilst the halogen substituted phenyl azoimides and diphenyl-4 : 4′-bisazoimide yield similarly the corresponding ethyl esters as primary products. *Ethyl* 1-(2 : 4-*dichlorophenyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylate*, m. p. 270° (decomp.), yields on hydrolysis the free *acid*, m. p. 169·5° (decomp.); 1-(2 : 5-*dichlorophenyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid* has m. p. 158°; *ethyl* 1-(2 : 4-*dibromophenyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylate*, m. p. 302° (decomp.), yields the free *acid*, m. p. 173°; 1 : 1′-(4 : 4′-*diphenylyl*)*bis*-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid* has m. p. 245° (decomp.). The following 1 : 2 : 3-*triazoles* were prepared by heating the corresponding 4-carboxylic acids above their melting points: 1-(2 : 4-*dichlorophenyl*)-5-*methyl*-, m. p. 69°; 1-(2 : 5-*dichlorophenyl*)-5-*methyl*-, m. p. 51°; 1-(2 : 4-*dibromophenyl*)-5-*methyl*-, m. p. 87°; and 1 : 1′-(4 : 4′-*diphenylyl*)*bis*-5-*methyl*-1 : 2 : 3-*triazole*, m. p. 227°. Phenyl-1 : 2 : 3-triazoles unsubstituted in the triazole ring have strong, mushroom-like odours, whilst the corresponding 5-methyl derivatives are odourless. F. G. W.

Relationship between Atomic Grouping and Specific Affinity. II. Diphenylcarbazone, its Salts, and those of the supposed Diphenylcarbodiazone. F. Feigl and A. F. Lederer (*Monatsh.*, 1924, 45, 63—68).—" Diphenylcarbodiazone " is regarded as a second form of diphenylcarbazone, and the structure of the isomerides and their salts is discussed. Certain discrepancies and anomalies are pointed out and theories of the constitution of the metallic salts of diphenylcarbazone and diphenylcarbodiazone are discussed (Cazeneuve, A., 1900, i, 465; 1901, i, 297). From diphenylcarbazone (I) salts are derived by replacing the hydrogen atom of the anilino group by univalent metal. Cazeneuve's



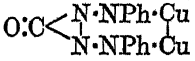
$\mathrm{O{:}C}<\begin{matrix}\mathrm{NH\cdot NHPh}\\ \mathrm{N{:}NPh}\end{matrix}$

(I.)



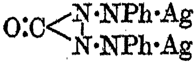
$\mathrm{O{:}C}<\begin{matrix}\mathrm{NH\cdot NPh}\\ |\\ \mathrm{NH\cdot NPh}\end{matrix}$

(II.)



$\mathrm{O{:}C}<\begin{matrix}\mathrm{N\cdot NPh\cdot Cu}\\ |\qquad\quad |\\ \mathrm{N\cdot NPh\cdot Cu}\end{matrix}$

(III.)



$\mathrm{O{:}C}<\begin{matrix}\mathrm{N\cdot NPh\cdot Ag}\\ |\\ \mathrm{N\cdot NPh\cdot Ag}\end{matrix}$

(IV.)

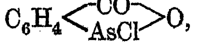
directions for preparing diphenylcarbodiazone, m. p. below 100°, led to a product, m. p. 164° with explosion, which is considered to be a cyclic diphenylcarbazone (II). III represents a salt with a bivalent metal, and IV the likewise unstable silver salt.

F. M. H.

Organic Compounds of Arsenic. I. Carboxylated Aromatic Arsinic Acids and Arseno Compounds. E. MASCHMANN (*Ber.*, 1924, **57**, [*B*], 1759—1766).—5-*Amino*-o-*tolylarsinic acid*, m. p. 235—236° (decomp.) after darkening at 200°, is prepared by reducing 5-nitro-*o*-tolylarsinic acid with ferrous sulphate and sodium hydroxide at 80°. 5-*Nitro*-o-*carboxyphenylarsinic acid*, m. p. 264—265° (decomp.) after darkening at 210°, obtained by the oxidation of 5-nitro-*o*-tolylarsinic acid by potassium permanganate, is reduced by sodium amalgam and methyl alcohol to 5-*amino*-o-*carboxyphenylarsinic acid*, m. p. 219—220° (decomp.), which is converted by nitrous acid into 5-*hydroxy*-o-*carboxyphenylarsinic acid*, decomp. indefinite. 5-Amino-*o*-tolylarsinic acid is diazotised and the diazonium solution is treated with cuprous cyanide; the nitrile thus obtained is hydrolysed by potassium hydroxide to 5-*carboxy*-o-*tolylarsinic acid* which remains unchanged below 300°. The compound is oxidised by potassium permanganate in alkaline solution to 2 : 5-*dicarboxyphenylarsinic acid*, decomp. indefinite. 5-Carboxy-*o*-tolylarsinic acid is converted by sulphuric acid and nitric acid (*d* 1·4) at 0—10° into 3-*nitro*-5-*carboxy*-o-*tolylarsinic acid* which is unchanged below 300°; it is reduced by ferrous sulphate and sodium hydroxide to 3-*amino*-5-*carboxy*-o-*tolylarsinic acid*. 2-Nitro-*p*-toluidine is transformed by diazotisation and treatment of the diazonium solution with sodium arsenite into 2-*nitro*-p-*tolylarsinic acid*, m. p. 241—242° (decomp.), which is oxidised by potassium permanganate to 2-*nitro*-4-*carboxyphenylarsinic acid*, m. p. 226—227° (decomp.), from which 2-*amino*-4-*carboxyphenylarsinic acid*, decomp. 225—226° (the *acetyl* derivative is described), and 2-*hydroxy*-4-*carboxyphenylarsinic acid*, decomp. indefinite, are obtained in the usual manner. 2-Nitro-*p*-tolylarsinic acid is reduced by sodium amalgam and methyl alcohol to 2-*amino*-p-*tolylarsinic acid*, decomp. 185°. 5-Nitro-2-carboxyphenylarsinic acid is reduced by hypophosphorous acid and potassium iodide to 5 : 5′-*diamino*-2 : 2′-*dicarboxyarsenobenzene*; 5 : 5′-*dihydroxy*-2 : 2′-*dicarboxyarsenobenzene* and 3 : 3′-*diamino*-5 : 5′-*dicarboxy*-2′ : 2′-*dimethylarsenobenzene* are prepared in a similar manner. 4 : 4′-*Dicarboxy*-2 : 2′-*diaminoarsenobenzene* (the *hydrochloride* is described) is obtained by the action of stannous chloride and potassium iodide on 2-nitro-4-carboxyphenylarsinic acid.

H. W.

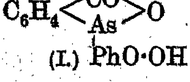
Organic Compounds of Arsenic. I. Derivatives of *o*-Benzarsinic Acid. J. A. Aeschlimann and N. P. McCleland (*J. Chem. Soc.*, 1924, **125**, 2025—2035).—When benzarsinic acid is reduced in aqueous solution by sulphur dioxide and a little hydriodic acid, the *hydrated* o-*benzarsenious oxide*, $CO_2H{\cdot}C_6H_4{\cdot}As(OH)_2$, is obtained, which melts at 89° and resolidifies at 140° with formation of the anhydride, $\left[C_6H_4{<}\substack{CO\\As}{>}O\right]_2O$, m. p. 231° after sintering at 225°. Anhydrous o-*benzarsenious oxide* is obtained by crystallising the hydrated compound from ether or benzene. It yields o-*benzarsenious chloride* when treated with hydrogen chloride in benzene or chloroform, and this, on distillation in a vacuum, affords o-*carboxyphenylchloroarsinous anhydride*,



$$C_6H_4{<}\substack{CO\\AsCl}{>}O,$$

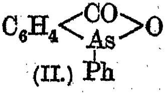
m. p. 145°, b. p. about 220°/15 mm., which is also obtained by distilling the product of the action of phosphorus trichloride on *o*-benzarsinic acid in chloroform. *Benzophenone*-o-*dichloroarsine*, $Bz{\cdot}C_6H_4{\cdot}AsCl_2$, m. p. 107—108°, was obtained from dichloro-*o*-arsinobenzoyl chloride (cf. Lewis and Cheetham, A., 1923, i, 407) and benzene using aluminium chloride in carbon disulphide. *Benzophenone*-o-*arsinic acid*, m. p. 215—219°, and *benzophenone*-o-*arsenious oxide*, m. p. 105—200° (incomplete), were obtained from the dichloroarsine by treatment with alkali and hydrogen peroxide, and alkali alone, respectively. By treating benzophenone-*o*-dichloroarsine with sodium hydroxide and methyl iodide, converting the resulting iodoarsine (m. p. 110—114°) into the oxide by means of alcoholic potassium hydroxide, and treating this with hydrogen chloride in benzene, *benzophenone*-o-*methylchloroarsine*, m. p. 88°, was obtained. Attempts to eliminate hydrogen chloride from this compound, by the action of aluminium chloride, failed. *Benzophenone*-o-*methylarsinic acid*, m. p. 186°, could not be dehydrated to form a ring compound.

o-*Carboxydiphenylarsinic anhydride* (I), m. p. not below 300°, was prepared by condensing benzenediazonium chloride with sodium benzarsinite. It is not affected by sulphuric acid at 100°. o-*Carboxydiphenylarsinous anhydride* (II), m. p. 133°, was obtained by reducing the above arsinic acid, and is also produced by the



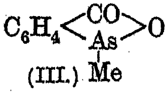
$$C_6H_4{<}\substack{CO\\As}{>}O \quad As{-}PhO{\cdot}OH$$

(I.)



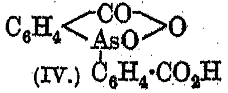
$$C_6H_4{<}\substack{CO\\As}{>}O \quad As{-}Ph$$

(II.)



$$C_6H_4{<}\substack{CO\\As}{>}O \quad As{-}Me$$

(III.)



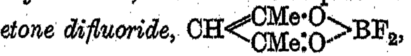
$$C_6H_4{<}\substack{CO\\AsO}{>}O \quad As{-}C_6H_4{\cdot}CO_2H$$

(IV.)

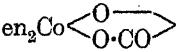
distillation, in a vacuum, of o-*carboxydiphenylchloroarsine*, m. p. 163°, prepared by condensing an alkaline solution of phenyldichloroarsine with diazotised anthranilic acid, reducing the product with sulphur dioxide, and treating the resulting acid with hydrogen chloride in benzene. On crystallising this compound (m. p. 163°) from benzene, a *product*, m. p. 125°, was obtained. The *acid chloride* of *o*-carboxydiphenylchloroarsine distils unchanged in a vacuum and partly crystallises. Treated with aluminium chloride, it yields benzophenone-*o*-dichloroarsine. o-*Carboxyphenylmethylarsinous anhydride* (III), m. p. 106°, b. p. 220°/15 mm., obtained by the action of methyl iodide and sodium hydroxide on benzarsenious oxide, yields o-*carboxyphenylmethylarsinic acid*, m. p. 310°, on oxidation, and this, on reduction and treatment of the reduction product with hydrogen chloride in benzene, affords o-*carboxyphenylmethylchloroarsine*, m. p. 141°, which loses hydrogen chloride on distillation in a vacuum. oo′-*Dicarboxydiphenylarsinic anhydride* (IV), m. p. 255°, obtained by condensing benzarsenious oxide with diazotised anthranilic acid, yields oo′-*dicarboxydiphenylarsinous anhydride*, m. p. 251—255°, on reduction, and this, on treatment with hydrogen chloride in methyl alcohol, affords oo′-*dicarbomethoxydiphenylchloroarsine*, m. p. 184°. F. G. W.

Residual Affinity and Co-ordination. XX. Chromic and Cobaltic Lakes of Mordant Azo-dyes. G. T. MORGAN and J. D. M. SMITH (*J. Chem. Soc.*, 1924, **125**, 1731—1739).—Eriochrome-red B (4-sulpho-β-naphthol-1 : 4′-azo-1′-phenyl-3′-methyl-5′-pyrazolone) contains one "chelate" group: it yields, with chromic fluoride, a *chromic* lake, and, with roseocobaltic chloride, first a *cobaltic* lake, then the *mono-* and *di-roseocobaltic* salts of the latter. Similarly, Palatine-chrome-black 6B (β-naphthol-1 : 1′-azo-β-naphthol-4-sulphonic acid) yields *chromic* and *cobaltic* lakes and the *diroseocobaltic* salt of the latter. Diamond-black PV (1 : 5-dihydroxynaphthalene-2 : 2′-azophenol-4′-sulphonic acid) yields a *chromic* lake, but with roseocobaltic chloride affords only the lake of the oxidised dye (8-hydroxy-α-naphthaquinone-7 : 2′-azophenol-4′-sulphonic acid) and its *mono-* and *di-roseocobaltic* salts. Metachrome-brown B (4 : 6-dinitrophenol-2-azo-*m*-toluylenediamine) gives a *cobaltic* lake. *o*-Carboxybenzeneazo-β-naphthol affords a *diroseocobaltic* salt of the cobaltic lake, and from *m*-acetylbenzeneazo-β-naphthol-6-sulphonic acid only the *triammonium monoroseocobaltic* salt is obtained. Constitutional formulæ for these compounds are discussed (cf. T., 1922, **121**, 2857, etc.). W. A. S.

Residual Affinity and Co-ordination. XXI. Boron β-Diketone Difluorides. G. T. MORGAN and R. B. TUNSTALL (*J. Chem. Soc.*, 1924, **125**, 1963—1967).—Boron trifluoride reacts with β-diketones, but unlike the trichloride yields no boronium salt, but a difluoride, in which there is no ionisable fluorine atom. Thus, with acetylacetone, reaction takes place and heat is evolved, *boron acetylacetone difluoride*,



$\mathrm{CH}{<}\genfrac{}{}{0pt}{}{\mathrm{CMe{\cdot}O}}{\mathrm{CMe{:}O}}{>}\mathrm{BF_2}$, m. p. 43°, is obtained. *Boron benzoylacetone difluoride*, m. p. 155°, and *boron dibenzoylmethane difluoride*, m. p. 191°, were prepared in a similar way. Analytical methods are described. W. A. S.

Residual Affinity and Co-ordination. XXII. Optically Active Salicylatocobalt Diethylenediammines. G. T. MORGAN and J. D. M. SMITH (*J. Chem. Soc.*, 1924, **125**, 1996—2004).—*Salicylatodiethylenediamminecobaltic chloride dihydrate*, $\mathrm{YCl(H_2O)_2}$, where Y is the complex  $en_2Co<\overset{O\text{---}}{\underset{O\cdot CO}{}}>C_6H_4$, was obtained as purplish-red plates by treating *trans*-dichlorodiethylenediamminecobaltic chloride with silver oxide and adding salicylic acid (1 mol.) to the filtrate. As a by-product, *disalicylatodiethylenediamminecobaltic salicylate*, $[en_2Co(C_7H_5O_3)_2]C_7H_5O_3$, was obtained as pale violet-pink needles. The *carbonato dihydrate*, $Y_2CO_3(H_2O)_2$, violet-red plates, was obtained from the above chloride by the action of silver carbonate, and was converted by treatment with *d*- and *l*-camphorsulphonic acids, respectively, into l-*complex*-d-*camphorsulphonate*, $YC_{10}H_{15}O_4S(H_2O)_2$, bright red plates, $[\alpha]_{Li_{6708}}$ −41·3°, $[M]_{Li}$ for the complex ion −290·4°, and d-*complex*-l-*camphorsulphonate*, $[\alpha]_{Li}$ +33°, $[M]_{Li}$ for the complex ion +242·1°. From these optically active salts the following were obtained by double decomposition: d- and l-*chloromercurate hydrates*, $[YH_2O]HgCl_3$, $[M]_{Li}$ +288° and −294·4°, respectively; and d- and l-*bromomercurate hydrates*, $[YH_2O]HgBr_3$, $[M]_{Li}$ ±294°. The racemic halomercurates form purplish-red plates of paler tint than the active isomerides, and are much less soluble in water. The active salts remain active if crystallised from boiling water, or left in solution for six weeks. The following racemoid salts are also described: *iodomercurate hydrate*, YH_2O,HgI_3, dark purple-red, flattened needles; *nitrate trihydrate*, $YNO_3(H_2O)_3$, dark red, deliquescent needles; *hydrogen dichloride trihydrate*, $YHCl_2(H_2O)_3$, scarlet, plates; *hydrogen dinitrate*, $YH(NO_3)_2$, dark red plates; and *hydrogen carbonate*, $YHCO_3$, bright red, diamond-shaped and six-sided plates. The retention of only one mol. of water or one hydrion in the complex ion is ascribed to the unique affinity of the one carbonyl oxygen of the complex. An analogous explanation is suggested for the formation of oxonium salts. F. G. W.

Relation of Chemical Structure to Rate of Hydrolysis of Peptides. I. Synthesis, Physical Constants, and Rates of Hydrolysis of Methylated Peptides. P. A. Levene, H. S. Simms, and M. H. Pfaltz (*J. Biol. Chem.*, 1924, 61, 445—464).—Glycylsarcosine, sarcosylglycine, and sarcosylsarcosine have been synthesised, their dissociation constants, isoelectric points, and relative rates of hydrolysis determined and compared with corresponding values for glycylglycine. (In the following, k_a represents the acidic dissociation constant, k_b that of the amino group.) *Glycylsarcosine*, from chloroacetylsarcosine and ammonium hydroxide, has m. p. 200—201°, k_a $1·48\times10^{-3}$, k_b $0·576\times10^{-5}$, isoelectric point p_H 5·68. *Sarcosylglycine*, from chloroacetylglycine and methylamine, has m. p. 195—197°, k_a $0·794\times10^{-3}$, k_b $0·537\times10^{-5}$, isoelectric point p_H 5·80. *Sarcosylsarcosine* has m. p. 180—185°, k_a $1·38\times10^{-3}$, k_b $2·09\times10^{-5}$, isoelectric point p_H 5·98. Glycylglycine has k_a $0·759\times10^{-3}$, k_b $0·195\times10^{-5}$, isoelectric point p_H 5·59. The hydrolyses were conducted at 100° with 1 mol. equivalent of acid; under these conditions all except sarcosylsarcosine followed the [illegible] course of a bimolecular reaction; hydrolysis experiments [illegible] quantities of acid indicate that anhydride formation is probably the explanation of the anomalous behaviour of sarcosylsarcosine. C. R. H.

Anhydride Structure of Silk Fibroin. E. Abderhalden and E. Schwab (*Z. physiol. Chem.*, 1924, **139**, 169—180).—Among the products of the reduction, by sodium and alcohol, of silk peptone (obtained by hydrolysing silk fibroin with 70% sulphuric acid at incubator temperature) there have been isolated methylpiperazine, 3-*methyl*-6-*hydroxymethylpiperazine* (as *dihydrochloride*) and a compound which appears to be the *tetrahydrochloride* of the piperazine corresponding to an anhydride of the glycylalanylglycyltyrosine previously obtained by Fischer and Abderhalden (A., 1907, i, 737) from silk fibroin. For comparison with this compound the authors prepared 2 : 6-*di*-p-*hydroxyphenylmethylpiperazine* by the reduction of tyrosine anhydride; this piperazine gives a *hydrochloride*, m. p. 265°, and does not give Millon's reaction. By the hydrolysis of silk fibroin with cold 70% sulphuric acid, alanylserine anhydride and an *anhydride* (alanine, tyrosine, glycine, 1 : 1 : 2 mols., less water, 4 mols.) were obtained. The latter gave a negative ninhydrin reaction and a positive picrate test, whereas a similar compound obtained previously (*loc. cit.*) had these properties reversed. It is from the alanylserine anhydride, presumably, that the methylhydroxymethylpiperazine is formed. C. R. H.

Anhydride Structure of Proteins. E. Abderhalden and E. Komm (*Z. physiol. Chem.*, 1924, **139**, 181—204).—The fact that Jaffé's reaction for creatinine (A., 1886, 1056) is given by diketopiperazines in general has been confirmed by tests carried out on the anhydrides of numerous amino-acids and dipeptides; in all cases the reaction was positive in the case of the anhydride and negative with the original amino-acid or peptide. Similar results were obtained with the reaction of von Bittó using *m*-dinitrobenzene and *m*-phenylenediamine. These two reactions have been utilised to investigate the question of the occurrence in proteins of preformed diketopiperazines; in many proteins and in the peptones derived therefrom, it was possible to demonstrate the presence of such compounds. The significance of this result in relation to the theory of the constitution of proteins is fully discussed. Included in the paper is a severe criticism of the work of Ssadikov and Zelinsky (this vol., i, 1122). C. R. H.

Origin of the Humin formed during the Acid Hydrolysis of Proteins. R. A. Gortner (*Z. physiol. Chem.*, 1924, **139**, 95—96).—Polemical (cf. Edlbacher, this vol., i, 891). E. S.

Dakin's Method Applied to Edestin. T. B. Osborne, C. S. Leavenworth, and L. S. Nolan (*J. Biol. Chem.*, 1924, **61**, 309—313).—Dakin's butyl alcohol method of extraction (A., 1919, i, 150) has been modified by dropping the concentrated solution of amino-acids into 7 volumes of butyl alcohol, which is rapidly stirred at the ordinary temperature. The products of hydrolysis of edestin were investigated by this method; no evidence could be obtained of the presence of β-hydroxyglutamic acid, which, in view of the fact that edestin may serve as the sole source of protein in a satisfactory diet for young rats, indicates that this amino-acid is not essential for growth. Part of the dry residue of the butyl alcohol extract was soluble in ethyl alcohol and appeared to consist of diketopiperazines. C. R. H.

Basic Amino-acids Yielded by Casein. C. S. Leavenworth (*J. Biol. Chem.*, 1924, **61**, 315—316).—The nitrogen, other than that of lysine, contained in the substances which can be precipitated by phosphotungstic acid from the products of hydrolysis of casein, amounts to 1·1% of the total nitrogen of the casein; it is therefore improbable that casein contains any hitherto unidentified basic amino-acid. C. R. H.

Correlation between the Spectra of various Hæmoglobins and their Relative Affinities for Oxygen and Carbon Monoxide. M. L. Anson, J. Barcroft, A. E. Mirksy, and S. Oinuma (*Proc. Roy. Soc.*, 1924, **B**, **97**, 61—83).—The relation log K=0·05× span, in which K is the equilibrium constant of the equation $CO+HbO_2 \rightleftharpoons CO\text{-}Hb+O_2$ and the "span" is the difference, in Ångström units, between the positions of maximum intensity of the α-oxyhæmoglobin and carbon monoxide–hæmoglobin spectral bands, has been found to hold for the hæmoglobins from a number of mammals. The span varies from 43 to 56 units in different species and also in individuals of the same species; these variations appear to be due to the specificity of the globin portion of the molecule. The similar relation $\log 1/C_{T_1} - \log 1/C_{T_2} = 0{\cdot}049\ (A_{T_1} - A_{T_2})$ exists between the shift in the absorption bands and change in affinity of hæmoglobin for oxygen during change in temperature; C_{T_1} and C_{T_2} represent, at temperatures T_1 and T_2, respectively, the concentration of oxygen in solution when the hæmoglobin is half-saturated, and A_{T_1} and A_{T_2} the corresponding positions of maximum intensity of the α-bands. E. S.

Hexagonal Crystals of Horse Hæmoglobin. E. Möllenhoff (*Z. Biol.*, 1924, **82**, 153—154).—Hexagonal crystals can be obtained without putrefaction taking place. The action which takes place during putrefaction is considered to be one of reduction. O. O.

The Carbohydrate Group of Thymus-nucleic Acid. H. Steudel and E. Peiser (*Z. physiol. Chem.*, 1924, **139**, 205—211; cf. this vol., i, 439).—The "glucal" reactions of Feulgen (A., 1914, i, 1098; 1918, i, 85; this vol., i, 1132) for thymus-nucleic acid are due to the elimination from the carbohydrate part of the molecule of 2-hydroxymethylfurfuraldehyde; these reactions are not given by dextrose itself, but are obtained (especially the green pine-shaving reaction) with more or less intensity in the cases of some di- and poly-saccharides and glucosides. The variations in the reactions are apparently due to differences in the linking of the carbohydrate portion to the rest of the molecule. C. R. H.

Biochemistry.

Muscular Exercise, Lactic Acid, and the Supply and Utilisation of Oxygen. IV—VI. A. V. Hill, C. H. N. Long, and H. Lupton (*Proc. Roy. Soc.*, 1924, **B**, **97**, 84—138).—IV. *Methods of studying the respiratory exchanges in man, during rapid alterations produced by muscular exercise, and while breathing various gas mixtures.*—The Douglas bag is considered more satisfactory than the closed gas chamber. The technique of the method is discussed with special reference to gaseous mixtures containing a high proportion of oxygen. Where the mixtures contain more than 50% of oxygen serious errors are liable to occur.

V. *The recovery process after exercise in man.*—After moderate short-lived exercise recovery is rapid and practically complete in a few minutes. This is due to the oxidative removal of lactic acid in the muscles where it was formed. After severe or prolonged exercise, the same initial rapid phase occurs, but this is followed by a protracted process, which represents the oxidative removal of lactic acid which has had time (owing to an inadequate oxygen supply) to diffuse from the muscles. These facts enable a distinction to be made between "moderate" exertion, which is followed by the initial phase only, and "severe" exertion, which is followed by both phases. During the early stages of recovery after severe exercise there is an elimination of carbon dioxide and a high respiratory quotient; during the later stages, a retention of carbon dioxide and a low respiratory quotient. The carbon dioxide so retained was used as a measure of lactic acid removed, and the oxygen used in recovery as a measure of the energy used in the removal of the acid. From these two quantities the "efficiency" of recovery in man has been calculated and found to agree with the value obtained for isolated frogs' muscle and also with that found by the amount of the lactic acid removed during any recovery interval compared with the recovery oxygen used in that interval. The time course of the recovery process while breathing oxygen-enriched air is not appreciably different from that while breathing atmospheric air, and the main process of recovery is practically unaffected by the higher oxygen pressures.

VI. *The oxygen debt at the end of exercise.*—Only about 5% of the oxygen debt is due to the extra circulatory and respiratory effort associated with recovery. It is considered that the remainder is utilised in restoring lactic acid to its precursor. The breathing of oxygen mixtures allows a considerable increase in the maximum oxygen debt. (Cf. this vol., i, 1128.) O. O.

Content of Sodium Chloride in the Blood of certain Marine Invertebrates. M. Duval (*Compt. rend.*, 1924, **179**, 706—708).—The blood of various marine invertebrates, especially of the crustaceans, contains appreciably less sodium chloride than the sea-water in which they are found. Equality between the osmotic pressures of the blood and of the water is effected by the other components of the blood. The blood of *Siponculus nudus*, however, contains exactly the same proportion of sodium chloride as sea-water. T. H. P.

Changes in Blood Electrolytes in Ether Acidosis. J. H. Austin, G. E. Cullen, H. C. Gram, and H. W. Robinson (*J. Biol. Chem.*, 1924, **61**, 829—840).—In the acidosis following ether anæsthesia there is, in the blood, a rise in the concentration of chloride ion, a fall in that of hydrogen carbonate, and a slight fall in that of the total base. These observations are, in themselves, insufficient to account for the increase in hydrogen-ion concentration which is simultaneously observed, and necessitate the hypothesis that the increased acidity is brought about by the presence of other unidentified anions. The authors suggest the liberation of lactic acid in the tissues as a possible cause of the phenomenon. (In this connexion, cf. Ronzoni, Koechig, and Eaton, this vol., i, 1258.) C. R. H.

Experimental Alterations in the Calcium Content of Human Serum and Urine. C. P. Stewart and J. B. S. Haldane (*Biochem. J.*, 1924, **18**, 855—857).—The calcium content of human serum can be raised by 10 to 20% by ingestion of calcium and ammonium chlorides, by breathing 6 to 7% carbon dioxide, or by forced breathing. It can be lowered by 10 to 20% by ingestion of sodium hydrogen carbonate. The urinary calcium output is increased by ingestion of ammonium chloride and is little affected by sodium hydrogen carbonate. S. S. Z.

Changes in the Phosphorus Partition in Human Blood during Ammonium Chloride Acidosis. H. D. Kay (*Biochem. J.*, 1924, **18**, 1133—1138).—There is a rise in inorganic phosphorus during ammonium chloride acidosis. The "lecithin" or lipin phosphorus changes in a similar way in this condition. The organic acid-soluble phosphorus (*i.e.*, the organic fraction after precipitating the blood with trichloroacetic acid) shows an immediate fall at the outset followed by a slow return to normal after several days. This change takes place in the portion of the fraction which is resistant to hydrolysis by the bone enzyme. The significance of these changes is discussed. S. S. Z.

Chemical Changes in the Blood during Fasting and subsequent Re-feeding. S. Morgulis and A. C. Edwards (*Amer. J. Physiol.*, 1924, 68, 477—498).—During prolonged fasting, the non-protein and urea nitrogen of the blood of dogs usually increases, then remains constant, and finally increases again; the amino-acid nitrogen remains constant or suffers at first a slight temporary diminution; the uric acid of the blood increases progressively; the creatinine remains constant, but the creatine first diminishes and then rapidly rises. The sugar and chlorides, which diminish at first, increase again during the later stages. When the animals are once again fed, very extensive changes occur in the composition of the blood, which eventually reaches a normal condition.

A. A. E.

Chemical Changes in Blood of Dogs after Thyro-parathyroidectomy. I. Greenwald (*J. Biol. Chem.*, 1924, **61**, 649—657).—After removal of the thyroids and parathyroids of dogs there was found, during the resulting tetany, no change in the titratable alkali, sugar, or nucleotide nitrogen of the blood, a decrease in the calcium, and a slight increase in the acid-soluble phosphorus; in view of the marked decrease in the excretion of phosphates which follows parathyroidectomy, it appears that, in this condition, phosphorus must be deposited in the tissues.

C. R. H.

Amino-acid Content of the Blood and its Significance as a Test of Liver Function. M. von Falkenhausen (*Arch. exp. Path. Pharm.*, 1924, **103**, 322—328).—The results of determinations of the amino-acid content of human blood, both normal and pathological (including diseases of the liver), give no support to the view that the liver plays an important part in intermediary protein metabolism. Determinations of the amino nitrogen content of the blood following ingestion of amino-acids are of no value as tests of liver function. E. S.

Possible Significance of Hexosephosphoric Esters in Ossification. IV. Phosphoric Esters of the Blood. H. W. Goodwin and R. Robison (*Biochem. J.*, 1924, **18**, 1161—1162).—Two phosphoric esters were isolated from the blood. One of these reduces Fehling's solution and is lævorotatory. It is hydrolysed by the bone enzyme. The other does not reduce Fehling's solution and is not acted on by the enzyme. S. S. Z.

Rate of Elimination of Inorganic Salts from the Blood Stream. O. Barkus (*Amer. J. Physiol.*, 1924, **69**, 35—40).—After intravenous injection, chlorides disappeared from sheep's blood almost immediately, phosphates first rapidly and then slowly; results with sulphates were untrustworthy.

Chemical Abstracts.

Carbohydrate Metabolism. I. Variations in the Nature of the Blood-sugar. L. B. Winter and W. Smith (*Proc. Roy. Soc.*, 1924, **B**, **97**, 20—40).—Normal blood filtrates have a lower rotation than would be expected from their copper-reducing power on the assumption that the reducing substance present consists solely of an equilibrium mixture of α- and β-glucose; the rotation, however, slowly increases and in 3 to 4 days corresponds with the reducing power. Filtrates from the blood of diabetics, on the other hand, have a high rotation which remains constant or diminishes only slightly. After mild hydrolysis (dilute hydrochloric acid), the rotation and reducing power of the normal filtrates correspond, whilst this treatment increases the rotation without affecting the reducing power of diabetic filtrates.

After injection of either thyroid extract or adrenaline, the blood of rabbits resembles diabetic blood in the above respect, but behaves normally when these substances are injected successively, although there is an increase in total blood-sugar. The blood of rabbits in convulsions due to insulin has a low rotation and no reducing power; the convulsions are relieved by adrenaline alone or by a mixture of thyroid and adrenaline. The mechanism of the action of insulin is discussed. E. S.

Hyperglycæmia after Parenteral Administration of Protein. W. LAUFBERGER (*Z. ges. exp. Med.*, 1924, **39**, 487—494; from *Chem. Zentr.*, 1924, i, 2794).—Intravenous injection of minimal amounts of protein causes hyperglycæmia in rabbits. The course of the hyperglycæmia varies with the protein used. Caffeine does not cause an appreciable hyperglycæmia in spayed females. G. W. R.

Effect of Ultra-violet Light on the Content of Fat and Sugar in the Blood of Animals deprived of Vitamins. D. ALPERN (*Strahlentherapie*, 1923, **15**, 661—666; from *Chem. Zentr.*, 1924, i, 2887).—The water and sugar in the blood of normal animals increase as the result of ultra-violet radiation. Less marked results are obtained in the case of the fat content. There is generally an increase in the light petroleum and ethyl alcohol fractions without corresponding increase in the cholesterol content. The blood of animals deprived of vitamins exhibits the same changes. G. W. R.

Alcohol. I. Determination of Ethyl Alcohol in Blood. H. KIONKA and P. HIRSCH (*Arch. exp. Path. Pharm.*, 1924, **103**, 282—294).—The alcohol is removed from the blood by distillation at 40° under diminished pressure, using an efficient condensing arrangement, and its content in the distillate determined by means of an interferometer. E. S.

Alcohol. II. Alcohol Content of Human Blood in the Fasting Condition, and after Ingestion of Carbohydrates or of Small Amounts of Alcohol. G. KÜHN (*Arch. exp. Path. Pharm.*, 1924, **103**, 295—312).—Values varying between 0·0006 and 0·0051% were found for the alcohol content of the blood of fasting individuals. No regular variations in these values were observed following a carbohydrate meal. Ingestion of small amounts of alcohol (two glasses of beer) together with a meal poor in carbohydrates, however, produced uniform increases which reached a maximum in about an hour. E. S.

Effect of Cations on Red Blood-corpuscles. W. ASHBY (*Amer. J. Physiol.*, 1924, **68**, 250—261, 585—610, 611—621).—Chlorides of sodium, magnesium, calcium, strontium, and barium increase, and of potassium and lithium decrease the resistance of human red blood-corpuscles to hypotonic sodium chloride solution. It is suggested that potassium can combine with the substance of the corpuscle in a manner different from that of sodium. Changes produced by calcium and magnesium are not accounted for by loss of potassium. The red corpuscles of rabbit's, horse's, and pig's blood, having a high potassium content, behave similarly; those of cat's, dog's, and steer's blood, in which sodium predominates, are affected by univalent cations in the reverse manner, but as before with magnesium and calcium. It is argued that the distribution of sodium and potassium between cells and serum must be due to specific mutual relationships between the ion and cell-substance. CHEMICAL ABSTRACTS.

Changes in p_H of Blood with Coagulation. E. F. HIRSCH (*J. Biol. Chem.*, 1924, **61**, 795—805).—In the process of clotting blood becomes more acid, the average decrease in p_H observed being 0·09. It is suggested that the normal process of clotting may be brought about by changes in reaction following changes in the tension of carbon dioxide. C. R. H.

Blood Coagulation, Anti-coagulants, and Hæmolysis. J. W. PICKERING and F. E. TAYLOR (*Proc. Roy. Soc.*, 1924, **B**, **97**, 1—19).—A parallelism exists between hæmolysis and the inception (*i.e.*, the pre-clot phase) of the clotting of blood. Thus, potassium oxalate and sodium citrate inhibit the hæmolytic actions of heterologous sera, a specific hæmolysin, and cobra venom; this inhibition is removed by calcium chloride, which also restores coagulability. Too large a concentration of calcium chloride, however, inhibits hæmolysis, but it is also known to prevent coagulation. Other anti-coagulants (Witte's peptone, leech extract, neutralised thymus- and yeast-nucleic acids, novarsenol) which inhibit the pre-clot phase also restrain the hæmolytic actions of the above substances. Further examples are discussed in the original. These results are interpreted in favour of the theory of the coagulation of blood advanced by Pickering and de Souza (*Biochem. J.*, 1923, **17**, 747). E. S.

Hæmolytic Action of the Soaps. E. PONDER (*Biochem. J.*, 1924, **18**, 845—851).—The stearates, palmitates, and oleates are hæmolytic. The stearates are the least and the oleates the most active in this respect. The changes of shape of the erythrocytes are very similar to those produced by saponin and by bile salts. This lytic action of soaps is inhibited by the presence of serum, plasma, and a solution of hæmoglobin, especially in the case of oleates. If, however, these substances are added to the soap after this has been allowed to act on the cells a slight acceleration in the lytic action may be effected. Sodium and potassium soaps behave similarly. The time–dilution curves are logarithmic, whilst the time–temperature curves are hyperbolic. The percentage hæmolysis curve of sodium oleate (the only soap with which these observations can be made) is of the sigmoid type and shows, when suitable concentrations are used, a slight positive skewness. Solutions of the soaps tend to lose their hæmolytic power on keeping. S. S. Z.

Colorimetric Determination of Blood p_H at Body Temperature. A. B. HASTINGS and J. SENDROY, jun.—(See ii, 869.)

Determination of Gases in Blood and other Solutions by Vacuum Extraction and Manometric Measurement. I. D. D. VAN SLYKE and J. M. NEILL. **II.** C. R. HARINGTON and D. D. VAN SLYKE.—(See ii, 872.)

Determination of Carbon Dioxide in Serum in presence of Ether. J. H. AUSTIN.—(See ii, 873.)

Micro-determination of Proteins in Blood-serum. W. BERGER and L. PETSCHOCHER.—(See ii, 636.)

Determination of the Protein Fractions in Serum and Plasma. H. W. KNIPPING and H. L. KOWITZ.—(See ii, 636.)

Rôle of Phosphates in Carbohydrate Metabolism. I. Action of the Muscle Enzyme on the Organic Phosphorus Compounds of Blood. II. Effect of Insulin Administration on the Distribution of Phosphorus Compounds in Blood and Muscle. H. D. KAY and R. ROBISON (*Biochem. J.*, 1924, **18**, 1139—1151).—From experiments with muscle enzyme, which hydrolyses hexosediphosphoric but not hexosemonophosphoric ester, on the phosphoric esters of blood it is concluded that a hexosediphosphoric ester may be present in the blood; the evidence, however, is not entirely conclusive. The greater part of the organic phosphate of the blood, which is hydrolysable by the bone enzyme, is not hydrolysed by muscle (this vol., i, 904). Evidence is produced that after the administration of insulin organic phosphoric esters are synthesised in the corpuscles at the expense of the inorganic phosphate originally present in the blood plus additional phosphate drawn from other tissues. These esters are chiefly of the type not hydrolysed by the bone enzyme, but it is probable that sugar or a sugar derivative enters into their molecule, and on the basis of 1 mol. of dextrose per atom of phosphorus, the phosphoric acid thus esterified would account for nearly 40% of the sugar simultaneously disappearing from the blood. No changes are found in the amount of inorganic phosphate or total acid-soluble phosphorus in muscle, following insulin administration, but there is a marked increase (50%) in the amount of phosphoric esters ("lactacidogen-P") hydrolysed during 3 hours' autolysis of the macerated muscle at 38°. The phosphate for this increased "lactacidogen" is apparently drawn from the muscle. There is no evidence as to the origin of the carbohydrate portion of the molecule, but it accounts for more than seven times the amount of dextrose which disappears from the blood. S. S. Z.

Relationship of Phosphates to Carbohydrate Metabolism. I. Time Relationship of the Changes in Phosphate Excretion caused by Insulin and Sugar. S. S. SOKHEY and F. N. ALLAN (*Biochem. J.*, 1924, **18**, 1170—1184).—The administration of insulin to normal animals results in an immediate reduction in the excretion of inorganic phosphate and ammonia and in the titratable acidity of the urine. The nitrogen excretion in these circumstances increases in the first 6 hours after the administration of the insulin, whilst the excretion of creatinine is unaffected. The volume of the urine is usually diminished in the first 3- or 6-hour periods after insulin and is followed by a compensatory increase usually appearing in the post-hypoglycæmic period. The administration of sugar induced an increased excretion of phosphate, but a decrease in the excretion of nitrogen. The joint effect of insulin and sugar brings about a decrease in the phosphate and nitrogen excretion. The administration of acid does not alter the excretion of phosphate. The phosphorus excretion of diabetic dogs without insulin is very high. Administration of insulin causes a decrease in the excretion, then an increase, with return to the level for a normal dog. These changes are discussed and their significance is suggested.

S. S. Z.

Acid–Base Exchanges in Mammalian Voluntary Muscle. S. Andrews, F. Beattie, and T. H. Milroy (*Biochem. J.*, 1924, **18**, 994—1008).—In the expressed juice from frozen muscle there are present at least three systems which carry base in a readily disposable form, namely, the inorganic phosphates, the organic phosphate precursors, and the colloidal or protein salts. When lactic acid is produced as a result of heating the juice, the acid secures its base from all these systems, the buffering capacity depending especially on the base derivable from the hydrolysed organic phosphate precursor, and also from the constituents of the juice which do not pass into the ultrafiltrate. If there is no inorganic phosphate increment accompanying the acid production, the buffering capacity is diminished, as the sole base-carrying systems which are then in evidence are the pre-formed inorganic phosphates and the proteins. S. S. Z.

Antiketogenesis. V. Ketolytic Reaction. Action of Glycollaldehyde and of Glyoxal. P. A. Shaffer and T. E. Friedemann (*J. Biol. Chem.*, 1924, **61**, 585—623; cf. A., 1921, i, 754; 1923, i, 166).—Glycollaldehyde, like dextrose, has the power of accelerating the oxidation of acetoacetic acid by hydrogen peroxide in alkaline solution. The previous view that the ketolytic reaction consisted in the condensation of an intermediate oxidation product of dextrose with acetoacetic acid with the formation of a readily oxidisable product, led to similar experiments with glyoxal, which is known to be an intermediate product in the course of the oxidation of glycollaldehyde to formic acid. Owing, however, to the extreme rapidity with which glyoxal is oxidised in alkaline solution, it does not, under these conditions, condense with acetoacetic acid, and therefore cannot act ketolytically. It is therefore necessary to assume that the ketolytic power of glycollaldehyde is due to the condensation of the aldehyde itself with acetoacetic acid, probably by Knoevenagel's reaction (A., 1898, i, 446), the condensation being accelerated by the rapid oxidative removal of the product. The hypothesis is supported by a quantitative analysis of the products of the ketolytic reaction; this analysis further indicates that 2 mols. of acetoacetic acid condense with 1 mol. of glycollaldehyde. It is suggested that the ketolytic action of dextrose may similarly be due to the direct condensation of the hexose itself, by virtue of its aldehydic properties, with 2 mols. of acetoacetic acid. C. R. H.

Synthesis of Menthol-glycuronic Acid in the Rabbit. A. J. Quick (*J. Biol. Chem.*, 1924, **61**, 679—683).—After administration of small doses of menthol to rabbits almost 50% is excreted in the form of menthol-glycuronic acid; the amount conjugated decreases as the dose approaches the lethal amount. During prolonged administration of sub-lethal doses, the daily excretion of menthol-glycuronic acid remains practically constant. C. R. H.

Decomposition of Sugar in the Lungs. E. Sluiter (*Arch. Néerland. Physiol.*, 1924, **9**, 461—479).—Perfusion experiments with blood containing added dextrose show that the sugar content of the blood falls for a time and then remains nearly constant; the failure to fall to a lower level may be due to the change of p_H of the blood caused by the production of lactic acid, inhibiting further glycolysis. The amount of sugar disappearing is not proportional to its concentration in the blood, nor does it give rise to the theoretical quantity of lactic acid. H. J. C.

Influence of "Collargol Blockade" of the Liver on Intermediary Metabolism. Suganuma (*Biochem. Z.*, 1924, **144**, 141—146).—Observations have been made of the effect of intravenous injections of collargol on the hepatic functions of starving dogs. The secretion of bile is diminished but later returns to supra-normal levels. The sugar and amino-acid content of the blood are increased; the former, however, becomes sub-normal before returning to normal values. Collargol injection lowers the urea content of the blood. The rise in blood-sugar is ascribed to stimulation of the liver cells, whilst the decreased blood-urea follows on the inhibition of the "star" cells of Kupfer. J. P.

Relation of Arginine and Histidine to Growth. W. C. Rose and G. J. Cox (*J. Biol. Chem.*, 1924, **61**, 747—773).—Rats fed on a diet of which the sole source of nitrogen is completely hydrolysed casein grow at a slower rate than those fed on the unhydrolysed protein; if the hydrolysis products are treated with silver sulphate and barium hydroxide to remove arginine and histidine, the residual mixture of amino-acids does not suffice for growth or maintenance of weight. The addition of 0·1 g. of histidine monohydrochloride per 100 g. of food to the diet, which had been made deficient by the above treatment, restores its growth-promoting properties, whereas the addition of even large amounts of arginine does not do so. The latter observation is in contradiction to the conclusions of Ackroyd and Hopkins (A., 1917, i, 237) regarding the interchangeability of arginine and histidine in metabolism. C. R. H.

Comparative Ability of Deficient Proteins and Ammoniacal Organic Salts partially to Satisfy the Minimum Nitrogen Requirements. E. F. Terroine, P. Fleuret, and T. Stricker (*Arch. Intern. Physiol.*, 1923, **22**, 43—86).—During the administration of a nitrogen-free diet, preceded by injection of ammonium salts, the nitrogen excreted was of the same order as that obtained when gelatin had been given. The economy value resultant from ammonium salts when the minimum nitrogen reserve is used up is smaller than that from gelatin, probably on account of the presence of some amino-acids. The amount of nitrogen necessary for endogenous metabolism can be regarded as the sum of (*a*) the amount of "differentiated" nitrogen in the form of amino-acids, and (*b*) that of "undifferentiated" nitrogen (of ammonia), often masked by nitrogen of amino-acids or ammonium salts.

CHEMICAL ABSTRACTS.

Changes in the Lime Content of the Hen's Egg during Development. R. H. A. Plimmer and J. Lowndes (*Biochem. J.*, 1924, **18**, 1163—1169).—Shell-less eggs contain more than sufficient lime for the needs of the developing chick. The lime content of eggs increases during the development of the chick; it enters the egg from the shell. A similar increase occurs in pigeons' eggs during development. S. S. Z.

"Lecitiburin," a Lecithin from the Eggs of the Shark. H. P. Ponce (*Anál. Asoc. Quím. Argentina*, 1924, **12**, 5—12).—A note describing the preparation from the eggs of the shark of a lecithin, m. p. 70°, to which the name "lecitiburin" is given.

G. W. R.

Chemical Composition of Edible Viscera from Meat-producing Animals. W. C. Powick and R. Hoagland (*J. Agric. Res.*, 1924, **28**, 339—346).—Analyses are recorded of edible viscera of steers, pigs, calves, and lambs. In general, the food values depend mainly on the protein content. Livers corresponded closely with lean beef in nitrogen content, but other organs were inferior in this respect. With the exception of hearts, tongues, lungs, and stomachs, the organs examined usually contained more phosphorus than lean beef. [Cf. *B.*, 1924, 961.] A. G. P.

Determination of Glycogen in the Placenta. R. Clogne, (Mlle.) Welti, and M. Pichon (*Bull. Soc. Chim. biol.*, 1924, **6**, 788—790).—Determinations of placental glycogen by the method of Bierry and Gruzewska, and by an improved modification of this method, give values varying between 0·60 and 1·66%. J. P.

Cholesterol Content of the Bile, Blood, and Flesh of the Hippopotamus. J. A. Gardner (*Biochem. J.*, 1924, **18**, 777—784).—The bile of the hippopotamus contains both free and ester cholesterol to the extent of 0·47% of the solid matter. Small quantities of free and ester cholesterol were also found in the blood and in the flesh of this animal. S. S. Z.

Inositol. II. Synthesis of Inositol in the Animal Body. J. Needham (*Biochem. J.*, 1924, **18**, 891—904).—The animal body seems to possess the power of synthesising inositol. Rats fed on an inositol-free diet for 8 months contained the normal amount of free inositol. No diminution in the body-content of inositol was observed when a lasting and vigorous excretion of the compound was induced in rats subsisting on an inositol-free diet. S. S. Z.

Uric Acid in the *Pieridæ*: Quantitative Study. V. B. Wigglesworth (*Proc. Roy. Soc.*, 1924, **B**, **97**, 149—155).—In *Pieris brassicæ*, the wings of the male contain more uric acid than do those of the female. This difference is attributed to the greater size of the wing scales which cover the androconia of the male. The total amount of uric acid is unchanged during pupal life. The *Pieridæ* appear to differ from other families in the use to which uric acid is put rather than in the amount produced. O. O.

Bioluminescence. V. Luciferin of *Cypridina Hilgendorfii*. S. Kanda (*Amer. J. Physiol.*, 1924, **68**, 435—443).—The methyl-alcoholic extract of *Cypridina* is evaporated to a small volume, ethyl alcohol is added, the liquid filtered, and the filtrate evaporated to dryness. The residue is dissolved in distilled water saturated with hydrogen, and the luciferin is completely precipitated on saturation with ammonium sulphate. The precipitate after rapid drying is again extracted with water saturated with hydrogen, or with absolute methyl or ethyl alcohol. The luciferin, the presence of which is indicated by the production of light with *Cypridina* luciferase, gives Molisch's reaction, but neither Millon's nor the ninhydrin reaction. It is not precipitated by acids, alkalis, or salts other than ammonium sulphate; results obtained with alkaloidal reagents were not conclusive. A. A. E.

Circulation of Lead in the Organism Investigated by a Radio-chemical Method. I. A. Christiansen, G. Hevesy, and S. Lomholt (*Compt. rend.*, 1924, **179**, 291—293).—Lead hydroxide mixed with olive oil containing a little lamp-black and some radium-*D* was injected into rabbits and guinea-pigs. A diagram is given showing lead distribution in fæces, urine, and viscera together with that found at the point of injection. The proportion of lead found in the liver and fæces is greater whilst that in the kidneys and urine is less than in the case of bismuth. H. J. E.

Micro-determination of Silicon and its Concentration in certain Organs. G. Bertrand.—(See ii, 872.)

Determination of Cystein. Y. Okuda.—(See ii, 792.)

Determination of Cystine. Y. Okuda.—(See ii, 793.)

Mammary Secretion. V. I. Further Research on the Threshold and Effects of Protein "Excess." II. Quantitative Relation of Vitamin-*B* to Protein. G. A. Hartwell (*Biochem. J.*, 1924, **18**, 785—794).—A high proportion of protein in the diet of the lactating rat produces an abnormal condition in the young. There is, however, a quantitative relationship between protein and vitamin-*B* in the diet; if the latter is increased when the protein is increased no evil results ensue, but the rate of growth of the suckling is impaired. The function of vitamin-*B* is primarily concerned with the metabolism of protein or with the nitrogen part of the protein molecule. S. S. Z.

Mineral Content of Human Milk in Normal and Rachitic Families. S. V. TELFER (*Biochem. J.*, 1924, **18**, 809—813).—No appreciable differences were found in the composition of the milks of women whether the infants developed rickets or not. S. S. Z.

Organic Constituents of Saliva. H. UPDEGRAFF and H. B. LEWIS (*J. Biol. Chem.*, 1924, **61**, 633—648).—A modification of the technique of Folin and Wu (A., 1919, ii, 308) is described, which is suitable for the removal of proteins from saliva, and the average concentrations of the non-protein nitrogenous constituents of normal saliva have been determined and compared with corresponding figures for blood. The total non-protein nitrogen of saliva is 37% of that of blood, but the relationship between the individual constituents is different in the two fluids, *e.g.*, in saliva there is relatively much ammonia and urea and practically no amino-acid nitrogen. C. R. H.

Analysis of Urine. MAX WEINTRAUT (*Arch. Pharm.*, 1924, **262**, 360—368).—A discussion of the determinations necessary for diagnostic purposes, and of the results produced by various pathological conditions. B. F.

Exchanges of the Blood and the Excretion of Urobilin. G. KÜHL (*Arch. exp. Path. Pharm.*, 1924, **103**, 247—259).—Contrary to Whipple's view (*Arch. intern. Med.*, 1922, **29**, No. 6), the urobilin excreted in the urine and fæces is derived solely from the destruction of hæmoglobin. When injected into normal dogs, hæmoglobin is converted quantitatively into urobilin and excreted as such; in anæmic animals, however, part of the hæmoglobin is retained. Following loss of hæmoglobin (withdrawal of blood), the excretion of urobilin falls below the normal. E. S.

Photochemical Reaction of Urine. A. VON SOÓS (*Z. klin. Med.*, 1924, **98**, 347—352; from *Chem. Zentr.*, 1924, i, 2789).—In dark urines, substances are found which inhibit the action of photographic developers on silver chloride which has been exposed to light. This effect is attributed to protective colloids. G. W. R.

Effect of Alcoholic Extract of Commercial Dextrose on Urinary Reducing Substance. C. C. WANG and A. R. FELSHER (*J. Biol. Chem.*, 1924, **61**, 659—665).—Ingestion of commercial dextrose causes a greater excretion of reducing substances than does the same weight of pure dextrose; the effect is due to an unidentified constituent of the commercial preparation which can be extracted therefrom with alcohol. The extract alone produces no excretion of reducing substance. C. R. H.

Rapid Determination of Lead in Urine. L. J. FAIRHALL.—(See ii, 873.)

Determination of Mentholglycuronic Acid in Urine. A. J. QUICK.—(See ii, 876.)

Direct Nesslerisation Micro-Kjeldahl Method and a Modification of the Nessler–Folin Reagent for Ammonia. F. C. Koch and T. L. McMeekin.—(See ii, 871.)

Glycolytic Properties of the Cancer Cell. N. Waterman (*Arch. Néerland. Physiol.*, 1924, **9**, 573—587).—Warburg's observation that the glycolytic power of carcinoma tissue from a rat was abnormally high has been confirmed for several types of tumour (man and rats) by measuring the carbon dioxide displaced from a Ringer solution containing added dextrose and excess of sodium hydrogen carbonate. The effect of calcium salts on this glycolysis has been studied and the lactic acid produced has been determined. It is found that normal pancreatic tissue from several types of animal possesses a definite though much smaller power to convert sugar into lactic acid. Attempts to raise the glycolytic power of normal tissue to the high level of that of tumour tissue (kidney tissue with its very low glycolytic power was used) were made; addition of phosphates to the Ringer solution was without effect: hexosephosphate gave inconclusive results; extraction of triturated carcinoma tissue with physiological saline and addition of the extract to the medium caused a rise in glycolytic action in some cases. H. J. C.

Calcium Content of the Blood-serum in Cases of Gout. V. Coates and P. C. Raiment (*Biochem. J.*, 1924, **18**, 921—924).—There is a considerable rise in the calcium of the blood-serum in cases of gout. S. S. Z.

Chemical and Physico-chemical Changes in Blood in Experimental Nephritis. J. Mosonyi (*Z. klin. Med.*, 1924, **99**, 500—505; from *Chem. Zentr.*, 1924, i, 2788).—After poisoning with cantharidin, the elimination of nitrogen in dogs remains normal. The freezing point of the blood rises to —0·512° and then sinks gradually to normal. After uranium poisoning, marked nitrogen retention occurs and the freezing-point of the blood rises to —0·53°, then falls to —0·638°, and subsequently becomes normal after repeated small rises. Mercuric chloride poisoning causes at first an increase in the nitrogen content of the blood. After 7 days, the residual nitrogen falls considerably below normal, and remains at this level until the end of the illness. G. W. R.

Nephropathic Action of the Dicarboxylic Acids and their Derivatives. I. Tartaric, Malic, and Succinic Acids. II. Glutaric and Malonic Acids. W. C. Rose (*J. Pharm. Exp. Ther.*, 1924, **24**, 123—146, 147—158).—The acids were administered subcutaneously to rabbits and their effect on renal activity determined by analyses of the blood constituents and by the phenolsulphonephthalein test; in a few cases, histological examinations of the kidneys were made. Tartaric and glutaric acids exerted a pronounced, and *dl*-malic acid a slight nephropathic action, while *l*-malic, succinic, and malonic acids were inactive. The renal-toxic action of certain acids appears to be associated with their slow oxidation in the organism. From the fact that calcium glutarate has a greater solubility than calcium succinate it is concluded that the toxicity of the glutarates is not due to the deposition of the insoluble calcium salt in the kidney. E. S.

Relation of the Fat-soluble Factor to Rickets and Growth in Pigs. III. S. S. Zilva, J. Golding, J. C. Drummond, and V. Korenchevsky (*Biochem. J.*, 1924, **18**, 872—880).—Rickets characterised by the presence of significant amounts of osteoid tissue can be induced in pigs on a diet in which dried separated milk is the main source of the fat-soluble vitamins. S. S. Z.

Chemical Basis for the Treatment of Tuberculosis. Action of Steapsin and Insulin on Tubercle Bacilli. L. G. Robinovitch and G. W. Stiles (*Amer. Rev. of Tuberculosis*, 1924, **9**, 587—612).—Lipase in alkaline solution to which is added a "co-hydrolyser" of bees-wax (chloroform), acts as a decorticator of tubercle bacilli, presumably by hydrolysing the lipoid outer membrane. Insulin produces the same effect as lipase. J. P.

Action of Alkaloids on the Field-locust (*Acridides*). R. Becker (*Arch. exp. Path. Pharm.*, 1924, **100**, 335—348).—The pharmacological actions of alcohol, ethereal oils, chloroform, xylene, benzene, acids, alkalis, and salts on the female of the field-locust are briefly recorded. At greater length are described investigations on the action of alkaloids, including physostigmine, veratrine, cocaine hydrochloride, nicotine, caffeine–sodium salicylate, morphine hydrochloride, arecoline hydrobromide, pilocarpine hydrochloride, and also of mixtures of these alkaloids. Similar effects to those obtained by the alkaloids, *i.e.*, paralysis, vibration of the jumping legs, etc., are obtained by the application of heat. W. O. K.

Action of Chemical Irritants on the Vitality of Protozoa, as Measured by the Rate of Division. H. Handovsky, E. du Bois-Reymond, and C. M. von Strantz (*Arch. exp. Path. Pharm.*, 1924, **100**, 273—287).—Cantharidin, undecylenylvanillylamide, amyl nitrite, and arsenious oxide usually inhibit the rate of division of *Balantiophorus minutus*. Histamine hydrochloride inhibits it at first and then later accelerates it. Cantharidin and arsenious oxide appear occasionally to have a stimulating action on some of the cells of a culture. W. O. K.

Action of Some Compounds on the Excitability of the Nervus Ischiadicus of the Frog. H. Handovsky and R. Zacharias (*Arch. exp. Path. Pharm.*, 1924, **100**, 288—293).—Morphine hydrochloride, chloral hydrate, alcohol, urethane, camphor, cocaine hydrochloride, veratrine, strychnine nitrate, and hydrogen peroxide increase in low concentration and decrease in high concentration the excitability of the nervus ischiadicus of the frog. Phenol, antipyrine, and novocaine were depressants, and caffeine an excitant, at all concentrations tested. Arsenious oxide was without effect. The inorganic ions present also influence the excitability, the potassium ion tending to increase it. W. O. K.

Leucocytogenic Properties of Copper Potassium Cyanide. E. Trocello (*Rassegna Clin. Terap. Sci. aff.*, 1923, **22**, 148—167; from *Chem. Zentr.*, 1924, i, 70).—Intravenous injection of a 0·2% aqueous solution of "cuprocyan" results in an increase in the number of leucocytes in the blood of rabbits. The effect is partly shown by the lymphocytes. G. W. R.

Pharmacological Investigations on Iron: Colloidal Ferrous Sulphide prepared in Presence of Gelatin. II. Experiments on Rabbits by Intravenous Injections. L. Sabbatani (*Atti R. Accad. Lincei*, 1923, [v], **32**, ii, 473—479).—The effects on rabbits of intravenous injections of the colloidal ferrous sulphide prepared by the method previously elaborated (this vol., ii, 116) are described. Whether *in vitro* or *in vivo* or in tissues isolated from the dead body, the sulphide passes into hydrated ferric hydroxide, which remains tenaciously held at the point where the sulphide was first fixed and is difficult to observe, as its colour is easily confused with that of the tissues themselves. T. H. P.

Pharmacological Investigations on Iron. V. Colloidal Ferrous Sulphide prepared in Presence of Gelatin. L. Sabbatani (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 8—13; cf. this vol., ii, 116, and preceding abstract).—Details are given of the effects produced in dogs by intravenous injection of colloidal ferrous sulphide prepared in presence of gelatin. T. H. P.

Induced Oxidation and the Explanation of the Internal Use of Iron Salts and of Fever. N. R. Dhar (*J. Physical Chem.*, 1924, **28**, 943—947).—The induced oxidation of fats, proteins, sugars, etc. by air at the ordinary temperature in the presence of sodium sulphite or of freshly-precipitated ferrous hydroxide (T., 1917, **111**, 690; A., 1921, ii, 36, 37, 391; 1922, i, 1210) is regarded as a close analogue of the processes which occur in the body. Fever is described as an auto-catalytic reaction accelerated by foreign substances, *e.g.*, bacterial secretions. S. S.

"Nitritoid Crisis" Produced by Arsenobenzene Derivatives. VI. Experiments on Isolated Organs with Plain Muscle. A. Busacca (*Arch. Farm. sperim. Sci. aff.*, 1924, **23**, 58—71).—Neosalvarsan in 0·01% solution is without effect on vascular musculature of isolated lung, which is without sympathetic innervation. In 0·01% solution, it produces enlargement of the pupil of the isolated eye of a frog, whilst at higher concentrations it acts as a local caustic and produces constriction. In 0·02% solution neosalvarsan and oxidised neosalvarsan stimulate motility in the plain muscle of certain human organs. With higher doses this effect is maintained in the case of neosalvarsan, whilst in the case of oxidised neosalvarsan, a depressant effect is produced. Neosalvarsan in therapeutic doses stimulates the terminal fibres of the sympathetic system, and it is suggested that this system is involved in the "nitritoid crisis." G. W. R.

Toxicity of Chaulmoogra Oil. B. E. READ (*J. Pharm. Exp. Ther.*, 1924, **24**, 221—258).—Ethyl hydnocarpate causes the same disturbances as the oil and hydnocarpic acid as the ethyl or glyceryl ester, or salt, appears to be the most active constituent of preparations of the oil. Toxic doses of hydnocarpates cause hæmolysis, renal irritation, and fatty infiltration of the liver. Increased lymph flow follows intravenous injection of ethyl hydnocarpate. Administered in this way, it kills rabbits in a dose of 0·5 c.c. per kg. body-weight, causing hypersensivity with lowered blood calcium, inco-ordinated movements, and finally death from respiratory failure. H. J. C.

Theory of Narcosis. M. CLOETTA and H. THOMANN (*Arch. exp. Path. Pharm.*, 1924, **103**, 260—281).—During narcosis with ether, alcohol, or "somnifen," the calcium content of the plasma of dogs is depressed (8—15%), the depression running parallel with the narcosis; corresponding with this depression, the potassium content of the plasma is increased. On the other hand, excitation with *ac*-tetrahydro-β-naphthylamine produces a rise in the calcium content. In conformity with these results, injection of substances which precipitate calcium (oxalates, phosphates) decreases the action of the above narcotics, the phosphates being the more effective in this respect. Administration of calcium increases the narcotic action in the case of frogs, but this effect has not been observed with dogs. No significant changes occur in the density, viscosity, or protein content of the plasma during narcosis, nor is the stability of the plasma colloids towards increases in temperature or changes in the concentration of ions altered; the surface tension, however, usually decreases slightly, but it is doubtful if this is of significance for narcosis. These results suggest that narcotics produce a disturbance in the ionic equilibrium in the brain and perhaps in other organs. E. S.

Narcotic Leucocytosis. Experimental Researches on Guinea-pigs. R. SEYDERHELM and E. HOMANN (*Arch. exp. Path. Pharm.*, 1924, **100**, 322—334).—Ether, chloroform, ethyl chloride, ethyl bromide, chloral hydrate, urethane, alcohol, sulphonal, and morphine, which induce narcosis when administered to a guinea-pig, also cause a marked leucocytosis in that animal, whilst scopolamine, which does not cause narcosis in the guinea-pig, does not give rise to a leucocytosis. There would therefore appear to be a definite leucocytosis, associated with the effect of drugs causing narcosis. W. O. K.

Comparative Toxicity of Novocaine, Neocaine, Procaine, and Apothesine. Effect of Intravascular Injections. W. R. MEEKER and E. B. FRAZER (*J. Pharm. Exp. Ther.*, 1924, **22**, 375—392).—Novocaine (German), and the corresponding products, neocaine (French) and procaine (American), have equal toxicity as determined by the minimum lethal dose on intravenous injection into rabbits under uniform conditions, and are equally effective as local or regional anæsthetics. The American product "apothesine" is more toxic. W. O. K.

Study of Two Series of Procaine Derivatives with Reference to the Relationship between their Pharmacological Action and Chemical Constitution. H. L. SCHMITZ and A. S. LOEVENHART (*J. Pharm. Exp. Ther.*, 1924, **24**, 159—166).—Determinations have been made of the relative anæsthetic activities and toxicities of various substituted aminoethanol and aminopropanol esters of *p*-aminobenzoic acid, using the rabbit's cornea for the former measurements, and mice for the latter. In both series, the anæsthetic activity increased with increase in the size of the substituent alkyl groups, the *iso*propyl compounds being more active than the *n*-propyl compounds. The toxicity, however, also increased. In the aminoethanol series this increase was proportional to the increase in anæsthetic activity, whilst in the case of the aminopropanol series it was greater than the anæsthetic activity. Hence, although the members of the latter series have greater anæsthetic activities than those of the former, their therapeutic indices are smaller.

E. S.

Local Anæsthetic Properties of *p*-Aminobenzoyldi*iso*propylaminoethanol Hydrochloride ("Isocaine"), Cocaine, Procaine, and Butyn. H. L. SCHMITZ and A. S. LOEVENHART (*J. Pharm. Exp. Ther.*, 1924, **24**, 167—177).—"Isocaine" has approximately the same efficiency as cocaine in anæsthetising the cornea and only three-tenths of its toxicity. It is twice as toxic as procaine, and hence is less suitable for paralysis of sensory nerve trunks, although it has about the same efficiency as the latter substance for this purpose. Butyn has ten times the toxicity of procaine; it is more efficient (but more toxic) than cocaine in anæsthetising the cornea, and only half as efficient as procaine for paralysis of sensory nerves. The minimum lethal doses of the drugs differ with different species. E. S.

Colloid Chemistry of Protoplasm. III. Viscosity of Protoplasm at Various Temperatures. IV. Heat of Coagulation of Protoplasm. L. V. HEILBRUNN (*Amer. J. Physiol.*, 1924, **68**, 645—648; **69**, 190—199).—III. Maximal viscosities were observed in the protoplasm of the egg of the clam *Cumingia* at 2°, 15°, and 30°.

IV. The temperature of coagulation of the protoplasm of sea urchin and *Cumingia* eggs is below that of proteins, but the coefficient is similar. The coagulation of protoplasm is probably associated with a change in the physical state of the emulsified fats.

CHEMICAL ABSTRACTS.

Biochemistry of Skin and the Chemical Basis of Skin Swelling. M. KAYE and D. J. LLOYD (*Biochem. J.*, 1924, **18**, 1043—1057).—There is an absolute identity of the conditions producing hardness in the interfibrillary fluid in which the fibrils and fibres of skin are embedded with those causing irreversible coagulation of proteins, and it is concluded that the cementing of the fibrils in some dried skins must be due to coagulation. Substances which disperse or destroy denatured albumin were also found to remove the coagulated interfibrillary matter. The colloidal swelling of skins is due to the network of skin fibres which consist of collagen, and the swelling in acid and in alkaline solution is brought about by the formation of ionisable salts of collagen. The removal of free amino groups in the skin reduces the amount of acid absorbed and combined. The swelling in acid solution is due to the presence of free amino groups. S. S. Z.

Nature of Fœtal Re-adsorption. N. H. Long and A. S. Parkes (*Biochem. J.*, 1924, **18**, 800—805).—Intra-uterine absorption of the fœtus is due to autolysis of the latter and not to the action of uterine enzymes. S. S. Z.

Autolysis. XII. Experimental Atrophy of Muscle Tissue. K. K. Chen, W. Meek, and H. C. Bradley (*J. Biol. Chem.*, 1924, **61**, 807—827).—During 9 weeks after section of the sciatic and femoral nerves in rabbits the muscles supplied by these nerves lost 50% in weight; they showed no increased water content. Such atrophic muscle contains the same amount of free amino-acids as healthy muscle and slightly more peptides; when subjected to sterile autolysis, it develops the same reaction as normal muscle but liberates more free amino-acids than the latter. It is suggested that this is due to a gradual alteration of the structural cell-proteins into a digestible form during the process of atrophy. C. R. H.

Effect of Heat on the Activity of the Peroxydase in Milk. G. Spitzer and M. C. Taylor (*J. Dairy Sci.*, 1924, 7, 234—244).—By use of the Storch reaction in comparative experiments on various mixtures of sterilised with raw milk, it was shown that the greater part of the peroxydase is inactivated at 85°. The rate of inactivation is a function of the temperature and time of exposure and appears to follow a definite law. Chemical Abstracts.

Laws of the Action of Laccase: Influence of the Reaction of the Medium. P. Fleury (*Compt. rend.*, 1924, **179**, 709—711; cf. A., 1924, i, 594, 697, 921, 1144).—The optimum value of p_H for the action of laccase varies from 6·7 to 7·6 as the percentage of guaiacol initially present in the solution varies from 1 to 0·25. The action of the laccase is regarded as the resultant of two phenomena, one being the fixation of the guaiacol by the enzyme and the other its oxidation; the former of these becomes less, and the latter more intense as the value of p_H increases. T. H. P.

Oxydases. J. Clarens (*Bull. Soc. chim.*, 1924, [iv], **35**, 1198—1206).—Using the constant-volume ureometer previously described (Job and Clarens, A., 1909, ii, 826), the oxidation of quinol in alkaline solution has been studied by measuring the rate of absorption of oxygen. The oxidation is proportional to the alkalinity of the solution and, owing to the formation of acid oxidation products, the oxidation ceases when the acidity reaches a certain value. If the acidity is removed by the addition of calcium carbonate, the oxidation continues at a rate determined by the velocity of reaction of the calcium carbonate with the acid oxidation products. The velocity of oxidation is increased by the presence of manganous salts. The acceleration is attributed to the power of manganese to form complexes with hydroxyl ions, thereby favouring the action of hydroxyl ions on the quinol in the presence of oxygen, a view supported by the fact that iron and copper salts similarly accelerate the oxidation. Oxidation in the presence of the oxydase of lucerne follows a different course. The oxidation products are not acid and the oxidation continues regularly; if the oxydase is destroyed by heat or by using very strongly alkaline solutions, the oxidation of the quinol continues until the alkalinity of the solution disappears owing to the formation of acid oxidation products, a certain number of hydroxyl ions being, however, immobilised in a complex with the the oxydase. This second mode of oxidation of quinol in presence of an oxydase is also catalysed by manganous salts. R. B.

Xanthine Oxydase. I. Preparation and Properties of the Active Material. M. Dixon and S. Thurlow (*Biochem. J.*, 1924, **18**, 971—975).—Xanthine oxydase is associated with the caseinogen of milk, and a stable preparation can be obtained by treating the milk with an equal volume of saturated ammonium sulphate solution. The precipitated caseinogen and fat are then dried between filter-paper, thoroughly extracted with ether, and the residue is dried. The enzyme can be adsorbed from a neutral solution of this preparation almost completely by alumina and filter-paper. Charcoal adsorbs it only slightly. It is destroyed by alcohol and acetone and slowly by atmospheric oxygen. Ether, chloroform, toluene, and glycerol do not inactivate it. The presence of fat in a finely-divided state, as in milk, accelerates the action of the enzyme. Hypoxanthine and xanthine on keeping in neutral solution become incapable of oxidation by the enzyme. S. S. Z.

Xanthine Oxydase. II. Dynamics of the Oxydase System. M. Dixon and S. Thurlow (*Biochem. J.*, 1924, **18**, 976—988).—The following results on the dynamics of xanthine oxydase have been obtained by employing the method of reducing methylene-blue to its leuco base in a vacuum. The reaction velocity is not affected by hydrogen-ion concentration between p_H 5·5 and 9. Above p_H 9 and below p_H 4, the enzyme is destroyed. Between p_H 4 and 5, the reaction velocity is very small, but no destruction occurs. The reaction velocity is directly proportional to the enzyme concentration, but is independent of methylene-blue concentration providing it is not very small. The reaction velocity is independent of purine-base concentrations up to a certain critical concentration, beyond which it decreases. This critical concentration becomes higher with increased enzyme concentration. Below the critical concentration of the substrate hypoxanthine reduces methylene-blue twice as fast as xanthine does, but as the inhibition begins the rates approach one another and become equal when inhibition is complete; the reaction velocity is then dependent on methylene-blue concentration. On addition of purines other than the substrate, the reaction velocity is also eventually decreased. The authors incline to the view that Schardinger enzyme and xanthine oxodase are identical. S. S. Z.

Xanthine Oxydase. III. Reduction of Nitrates. M. Dixon and S. Thurlow (*Biochem. J.*, 1924, **18**, 989—992).—The "atite" of Haas and Hill (this vol., i, 349) is identical with the oxydase or oxydases of milk. Xanthine oxydase reduces nitrates to nitrites in the presence of hypoxanthine, xanthine, adenine, or aldehyde. The rate of reduction of nitrate is proportional to that of the reduction of methylene-blue under various conditions. The inhibitory effect of purines is also observed in this case (see preceding abstract).

S. S. Z.

Phosphoric Esterase of Blood. M. Martland, F. S. Hansman, and R. Robison (*Biochem. J.*, 1924, **18**, 1152—1160).—The inorganic phosphate in the laked whole blood and in laked corpuscles increases rapidly at first and then more slowly, until after 4 days it amounts to 93% of the organic acid-soluble phosphorus in both cases. The rate of hydrolysis is greater at a p_H slightly on the acid side of the normal blood reaction and close to the neutral point. The enzyme responsible for the hydrolysis is present in both plasma and corpuscles or is possibly adsorbed by the latter from the plasma. It resembles the muscle esterase in its ability to hydrolyse hexosediphosphoric esters and in its relative inactivity towards hexosemonophosphoric and glycerophosphoric esters. A portion of the esters hydrolysable by bone is also hydrolysed by the blood enzyme during the early stages of autolysis, but the remaining portion is very resistant. It is found that no significant change in the reducing power occurred during the early stages of the autolysis in laked blood or corpuscles, although 50% of the phosphoric esters might be hydrolysed. In the later stages of the hydrolysis, a rise of about 30% in the sugar value is usually observed. In unlaked whole blood at a p_H somewhat above normal, synthesis of phosphoric esters was observed; when the p_H rises above or falls below certain limits, the rate of hydrolysis of the phosphoric esters becomes greater than the rate of synthesis and the inorganic phosphate increases. At a p_H somewhat lower than 7·0, the rate of hydrolysis may approach that in laked blood. S. S. Z.

***A*. Use of Invertase. *B*. Repeated Use of the Same Preparation of Invertase.** E. K. O. Schmidt (*Z. Ver. deut. Zuckerind.*, 1924, **817**, 727—780).—*A*.—A solution of invertase prepared by the autolysis of yeast can be concentrated at 30°/30 mm. without much loss of activity. A study of the effect of invertase on solutions containing different concentrations of sucrose shows that the time required to reduce the rotatory power of the solution to zero increases with the concentration of sucrose, somewhat more slowly than the latter up to 20% sucrose, and more quickly between 20% and 50% sucrose. The optimum temperature for the action of yeast invertase is about 55°. The less pure the sugar, the less active is the invertase.

B.—At 55°, at which temperature zymase is destroyed, whole yeast can be used for the inversion of sucrose; it is possible, after inversion is complete, to remove the yeast by filtering the solution through a collodion filter and use it for the inversion of a second lot of sucrose, or to make the process of inversion continuous by sucking the sucrose solution slowly through such a filter covered with a layer of yeast. Preparations obtained by the adsorption of invertase on charcoal are not suited for repeated use because the enzyme is readily dissolved out from the adsorbate, but the dried residue of a mixture of a solution of invertase with one of gelatin can be used for the inversion of at least eleven successive quantities of sucrose without loss of activity. C. R. H.

Mode of Action of Invertase. H. VON EULER and K. JOSEPHSON (*Arkiv Kemi, Min., Geol.*, 1924, **9**, No. 4, 1—6).—It is calculated that for invertase $k_a=10^{-7}$, $k_b=10^{-11}$, with the isoelectric point about $p_H=5$; viscosity measurements show a minimum at $p_H=$ 4—5. Reaction-producing molecules of catalyst+substrate are postulated, their formation and decomposition discussed, and their concentration is estimated at 10^{-8} for 0·1*N*-sucrose. The activity–p_H curve is said to be almost identical with that of raffinase on the alkaline side of the optimum. [Cf. *B.*, 1924, Dec. 26.]
F. M. H.

Properties of a Highly Active Invertase Preparation. K. MYRBÄCK (*Arkiv Kemi, Min., Geol.*, 1924, **9**, No. 2, 1—6).—A highly purified stable invertase (*If*=240) was prepared (cf. *B.*, 1924, Dec. 26) and was found to have no significant optical activity. Its acidity (cf. Michaelis, *Biochem. Z.*, 1915, **65**, 360) was half that of an albumin preparation but its basicity was about equal to that of the albumin (cf. Euler and Josephson, A., 1923, i, 721). The equivalent concentration of the invertase was found to be $1{\cdot}64\times10^{-3}$ in 1% solution, corresponding with an invertase equivalent of about 6000; $k_b=3\times10^{-10}$. F. M. H.

Polysaccharides. XXVII. Lichenase. P. KARRER and M. STAUB (*Helv. Chim. Acta*, 1924, **7**, 916—928; cf. this vol., i, 471).—Lichenase occurs in Plata-barley from the first to the eleventh day of germination. Its amount increases a little after the first day and then remains constant. It is present in nearly constant amount in spinach seeds both before and during germination. During the first few days of germination, the lichenase of maize is distributed equally between the embryo and the endosperm. Subsequently a greater proportion is found in the embryo. Green *Triticum repens* contains lichenase. The enzyme has been found in the intestine of a rabbit (cf. Tschermak, *Biochem. Z.*, 1912, **45**, 452), but all previous attempts failed to reveal it in the alimentary canal of any other vertebrate. It is now shown to be present in the stomach of the pig and of the cow, but not in the rennet-bag of the latter animal. Whether it originates in these places or is introduced along with the food is not certain. Lichenase is not present in the stomach of a calf which has been fed entirely on milk. The effect of additions on the enzymic hydrolysis of lichenin was studied at p_H 3·94—7·1. Dextrose, lævulose, galactose, maltose, sucrose, cellobiose, and gentiobiose inhibit the action; sodium chloride is inactive; the effect of egg-albumin varies with p_H, but is greatest in feebly acid solution.

Snail-lichenase after dialysis for many days contains no enzymes acting on starch, inulin, maltose, lactose, β-methylglucoside, or ethyl β-methylglucosidosalicylate, and invertase is present only in traces. On the other hand, the enzyme decomposes not only lichenin, but also cellobiose and gentiobiose. The decomposition of gentiobiose supports the theory that cellulose contains glucose residues attached by 1 : 6-glucosidic linkings. W. E. E.

Diastatic Power of the Juice of Different Varieties of Potatoes. A. JOSZT and B. STARCZEWSKI (*Rozpraw bjolog. z zakresu rolnictwa, hodowli i med. wet.*, 1922; from *Chem. Zentr.*, 1924, i, 2784).—Removal of nitrogenous substances from the juice of potatoes is not completely effected by heating, or by treatment with lead acetate, animal charcoal, or colloidal ferric hydroxide. To accomplish this it is necessary to add 1% ammonium sulphate after heating the juice for 10 minutes at 100°. Considerable differences are shown in diastatic power, but no marked relationship was found between the acidity of the juice, the starch concentration, and the degree of germination. G. W. R.

Influence of Hydrogen-ion Concentration on the Action of certain Amylases. J. T. GROLL (*Arch. Néerland. Physiol.*, 1924, **9**, 520—538).—Differentiation between various amylase preparations has been studied by comparing the types of curves obtained by plotting the time of hydrolysis of starch against the p_H of the buffered medium (methods are those of the author; cf. *ibid.*, 1918, **2**, 516; 1922, **6**, 445). The amylase of ox-blood acts best in an alkaline medium, p_H 8. The amylases of different organs or secretions of the same animal may vary considerably (in man, that of saliva and pancreas; cow, that of milk, blood, and pancreas), or be nearly the same (in man, pancreas and urine). In the same organs of different animals, a similar variation is found; *e.g.*, the amylase of human pancreas differs considerably from those of ox and pig pancreas which are very similar. H. J. C.

Allelocatalysis and the Growth of Yeast. G. L. PESKETT (*Biochem. J.*, 1924, **18**, 866—871).—Living yeast-cells grown in bacteria-free media in hanging-drop preparations, multiply in proportion to the number of cells present. The phenomenon of "allelocatalysis," *i.e.*, the mutual acceleration of reproductive rate by contiguous organisms, observed by Robertson (*ibid.*, 1921, **15**, 612) in the case of certain infusoria does not hold true in this case.
S. S. Z.

Cannizzaro's Reaction in the Mechanism of Alcoholic Fermentation. C. SCHWEIZER and H. GEILINGER (*Bull. Assoc. Chim. Sucr.*, 1924, **42**, 20—31).—The acetic acid and alcohol produced by the action of pressed yeast on acetaldehyde are formed in equivalent amounts, as required by Cannizzaro's reaction, only when oxygen is completely excluded from the reaction mixture.
E. S.

Specific Action of Plant Proteases. A. V. BLAGOVESCHENSKI (*Biochem. J.*, 1924, **18**, 795—799).—From experiments on the proteases of *Cannabis sativa*, *Phaseolus Mungo*, *Brassica rapa*, *Lupinus luteus*, *Hibiscus esculentus*, and *Dolichos melanophthalmus*, DC. the author concludes that the enzyme from every plant splits its own globulin more actively than the globulins of other plants.
S. S. Z.

Behaviour of Dried Enzymes on Exposure to Heat. III. Pancreatic Enzymes. C. ARTOM (*Arch. Farm. sperim. aff.*, 1924, **38**, 105—132).—Both the enzymes in the pancreas of the dog and those in the pancreatic juice itself, when dried at 10—30°, withstand higher temperatures in the dry state than after re-solution in water. This protective effect of drying is, however, considerably less marked in the latter than in the former of the two cases. These results correspond with those previously obtained with intestinal enzymes.
T. H. P.

Ammonia Production by Animal Tissues *in vitro*. I. Use of Mixed Tissue Extracts. J. M. LUCK (*Biochem. J.*, 1924, **18**, 814—824).—A series of experiments with mixed and single tissues is described. Free ammonia is liberated from trypsin-digested caseinogen by the liver and kidney, and very slightly by intestinal mucosa. It is considered to be due to deamidation and not to deamination. Urea was formed by preparations of the liver, intestinal mucosa, and kidney. Marked ammonia production was observed in mixtures of gastric mucosa and liver preparations. No appreciable deamination by either gastric mucosa or liver or other single tissue preparation could be demonstrated. Definite deamidation was effected by the liver, gastric mucosa, kidney, intestinal mucosa, and most liver mixtures. The liver and the liver-mixtures synthesise an amide-like substance. No residual amide nitrogen could be found after the action of a gastric mucosa–liver mixture on totally hydrolysed gelatin.
S. S. Z.

Ammonia Production by Animal Tissues *in vitro*. II. Demonstration of Urease in the Animal Body. J. M. LUCK (*Biochem. J.*, 1924, **18**, 825—828).—From experiments on a number of animals, it is concluded that the animal body contains urease. The gastric mucosa of the carnivora gave the most active preparations. The distribution of the enzyme in the stomachs of the ruminants is definite. The enzyme is present in the abomasum where peptic digestion takes place. No urease could be found in the gastric mucosa of the rodents.
S. S. Z.

Irregularities in Lactic Acid Fermentation. C. RICHET and H. CARDOT (*Ann. Inst. Pasteur*, 1924, **38**, 842—847).—It is shown that the irregularities observed by the authors in lactic acid fermentation in the presence of mercuric chloride as an antiseptic are dependent on the dilution of the inocula, being more marked at dilution 30,000 than at 300, whilst at a dilution of 300,000 the mercury-treated cultures do not ferment (cf. Lumière, A., 1923, i, 353).
J. P.

Regularity of Lactic Acid Fermentation. A. Lumière (*Ann. Inst. Pasteur*, 1924, **38**, 848—850).—Polemical in reply to Richet and Cardot (preceding abstract). J. P.

Influence of Media containing Bile on the Chemical Composition of *Bacillus subtilis*. A. Berthelot and E. Ossart (*Bull. Soc. Chim. biol.*, 1924, **6**, 770—772).—Cultures of *Bacillus subtilis* grown in media containing bile and afterwards dried, yield on acid hydrolysis a much smaller proportion of reducing substance (dextrose) than do cultures grown in the absence of bile. J. P.

Bacterial Nutrition. II. H. R. Whitehead (*Biochem. J.*, 1924, **18**, 829—832).—When broth is autoclaved some substances necessary for streptococcal growth are destroyed. These substances are contained in the fraction of the broth precipitable by phosphotungstic acid. This fraction alone, however, is not sufficient. Glycine, alanine, leucine, tyrosine, tryptophan, histidine, aspartic and glutamic acids do not remove this deficiency in the same way as does the filtrate after precipitation with phosphotungstic acid. Caseinogen broth was submitted to fractionation by Dakin's butyl alcohol extraction method, and it was found that the fractions soluble in butyl alcohol, in butyl and in ethyl alcohol, and the fraction insoluble in butyl alcohol did not promote streptococcal growth alone. Complete growth was obtained only when all the three fractions were reunited, although partial growth could be obtained with any two fractions. The fraction insoluble in butyl alcohol was active in high concentration. This was most probably due to incomplete extraction. S. S. Z.

Relation between the Chemical Composition of Peptones and Hydrogen Sulphide Production by Bacteria. F. W. Tilley (*J. Bact.*, 1924, **8**, 287—295).—Commercial peptones contain unoxidised, partly oxidised, and oxidised sulphur compounds. No hydrogen sulphide is liberated by bacteria from the last named, but freely from the others. Hydrogen sulphide is produced from cystine in abundance. Chemical Abstracts.

Fermentation of Salts of Organic Acids as an Aid to the Differentiation of Bacterial Types. H. C. Brown, J. T. Duncan, and T. Henry (*J. Hygiene*, 1924, **23**, 1—22).—The production of gas and change of reaction produced by bacteria in organic salt media are irregular and cannot be used as criteria for the differentiation of bacterial types. Suitable data can be obtained, however, because the decomposition of the salts of certain organic acids having insoluble lead salts can be demonstrated by adding lead acetate to the media after incubation (only formic of the simple monobasic and dibasic aliphatic acids is readily attacked; monohydroxycarboxylic acids are also stable but tartaric and citric acids are easily decomposed). Using the sodium salts of citric, *d*-, *l*-, and *r*-tartaric, fumaric, and mucic acids, seven different groupings of the common *Salmonella* types have been obtained (the usual sugar reactions give only four). The method has been applied to other groups of bacteria. Citric acid on bacterial decomposition by

B. suipestifer yields acetic and succinic acids and carbon dioxide; a reaction mechanism is suggested. Fumaric acid yields succinic acid. These organic salt fermentations cannot be used to replace the sugar reactions in general use. H. J. C.

Production of Organic Compounds of Sulphur in Bacterial Cultures with Special Reference to Glutathione. J. W. McLeod and J. Gordon (*Biochem. J.*, 1924, **18**, 937—940).—A distinct nitroprusside reaction was observed in 24—48-hour cultures of a number of anaërobes: *Bacillus paratyphosus* B and most allied species, *Cholera vibrio*, *B. typhosus*, *B. pyocyaneus*, and some strains of *B. coli* and *B. proteus*. No such reaction could be detected in cultures of *Staphylococcus*, *Streptococcus*, *Pneumococcus*, *Gonococcus*, *Meningococcus*, *B. influenzæ*, *B. Morax-Axenfeld*, *B. paratyphosus* A, or the dysentery bacilli. The thermostable substance reacting with nitroprusside is oxidised glutathione or some related compound originally present in the medium and reduced by the organisms in the course of their development. S. S. Z.

Selective Bactericidal Action. E. A. Cooper and G. E. Forstner (*Biochem. J.*, 1924, **18**, 941—947).—The chemical germicides, namely those that react with the constituents of protoplasm, have a more powerful action on *Bacillus coli* than on *B. pyocyaneus*. Formaldehyde forms an exception in this respect, attacking both organisms equally. Germicides, on the other hand, such as the aliphatic alcohols, phenol, etc., which exert a physico-chemical action on bacteria are more active towards *B. pyocyaneus* than towards *B. coli*, and their germicidal action in this case resembles that of heat. S. S. Z.

Chemotherapeutic Experiments with Chaulmoogra and Allied Preparations. IV. Growth-inhibiting Effect of Organic Compounds towards Acid-fast Bacilli. V. Mechanism of Growth-inhibiting Effect of Chaulmoogra and Other Vegetable Oils. O. Schöbl (*Philippine J. Sci.*, 1924, **25**, 123—134, 135—150).—IV.—In general, water-soluble organic antiseptics inhibit the growth *in vitro* of *Bacillus tuberculosis*, whereas fat solvents do not. The sodium, copper, and nickel salts of fatty acids are antiseptic; the zinc, strontium, lead, and uranium salts are inactive. The presence in a compound of an aliphatic double bond, a benzene nucleus, one or more phenolic groups, or an alkyl group attached to a benzene nucleus all tend to increase its antiseptic activity. The amino group in aromatic compounds has no influence if it is attached to the benzene ring but greatly increases the activity if it is in the side chain. Terpenes are less active than their related straight-chain compounds.

V.—Although the degree of unsaturation of vegetable oils does not run parallel with their power to inhibit or to promote the growth of acid-fast bacteria, yet complete hydrogenation abolishes their activity. In terms of Ehrlich's theory the author suggests that all the oils which have any effect on the growth of bacteria have a "haptophore" group by virtue of their unsaturation, and that the

nature of their effect depends on whether the rest of the molecule is a " toxophore " as in the case of chaulmoogra oil or a " nutriphore" as in the case of the growth-stimulating oils. The " nutriphore " in the latter case is the glycerol part of the molecule, the fatty acids being without effect. Some evidence was obtained of acquired tolerance on the part of the bacteria towards chaulmoogra oil.
C. R. H.

Extraction and Purification of Insulin. L. BANTI (*Arch. Farm. sperim. aff.*, 1924, **38**, 176—184).—Marked improvement in the yield of insulin obtained from pancreas is attained by addition of a relatively high proportion of acid to the alcohol used for the extraction, and by the employment of a procedure which gives highly concentrated aqueous solutions of insulin without evaporation in a vacuum. [Cf. *B.*, 1924, Dec. 26.] T. H. P.

Duality of Insulin. L. AMBARD, F. SCHMIDT, and M. ARNOVLYEVITCH (*Compt. rend. Soc. Biol.*, 1924, **90**, 790—792; from *Chem. Zentr.*, 1924, i, 2794).—Two insulin hormones are distinguished: one concerned in the oxidation of sugar to carbon dioxide and water, and the other polymerising sugar to glycogen. An equilibrium appears to exist between the two hormones whereby an increase in the one is associated with a decrease in the other.
G. W. R.

Efficiency of Various Sugars and their Derivatives in Relieving the Symptoms caused by Insulin in Mice. P. T. HERRING, J. C. IRVINE, and J. J. R. MACLEOD (*Biochem. J.*, 1924, **18**, 1023—1042).—Complete positive results were obtained with dextrose and mannose. Maltose was also permanently efficacious, but its action was slower. Temporary disappearance of symptoms was obtained with lævulose, galactose, and tetra-acetylfructose. Lactose, 2 : 3 : 5 : 6-tetramethylglucose, 2 : 3 : 5-trimethylglucose, sucrose, α- and β-methylglucosides, tetramethyl-β-methylglucoside, tetramethyl-γ-methylglucoside, glucose-monoacetone, salicin, mannitol, dulcitol, and β-glucosan had no action at all. The relation of chemical structure and some physiological considerations are discussed. S. S. Z.

Concentration-Action Curve of Insulin Preparations, and Anti-Insulin. S. G. DE JONGH (*Biochem. J.*, 1924, **18**, 833—838).—An anti-insulin substance was observed in some Dutch preparations which showed the phenomenon of double convulsant doses and differed in their behaviour in the case of rabbits and of diabetics. The concentration curve of insulin with regard to sugar seems to be a straight line, that of the anti-insulin an adsorption curve. S. S. Z.

Extraction and Properties of an Ovarian Hormone. E. A. DOISY, J. O. RALLS, E. ALLEN, and C. G. JOHNSTON (*J. Biol. Chem.*, 1924, **61**, 711—727).—Fresh liquor folliculi was mixed with alcohol and the solution evaporated to dryness after removal of the proteins; the residue was extracted with alcohol and the solution treated with acetone to remove phospholipins, this process being repeated several times; finally the dry residue from the alcoholic extracts was taken up in ether. Amounts of the order of a few mg. of the dry residue from this ethereal solution, when injected into ovariectomised rats, were found to induce the full œstrous cycle in these animals. The active substance is soluble in ether, alcohol, chloroform, light petroleum, or acetone, but insoluble in water. It is thermostable and moderately resistant to both acid and alkaline hydrolysis; it is not affected by tryptic digestion. Preparations with similar properties were obtained from placenta and from whole ovaries, but the yield of active substance was much smaller; no active preparations could be made from corpora lutea. C. R. H.

Durability of Vitamin-*A* of Cod-liver Oil. E. POULSSON (*Biochem. J.*, 1924, **18**, 919—920).—A sample of cod-liver oil 23 years old in daily doses of 3—5 mg. promoted growth in rats deficient in vitamin-*A*. S. S. Z.

Stability of the Vitamin-*A* of Cod-liver Oil Towards the Hardening Process. S. S. ZILVA (*Biochem. J.*, 1924, **18**, 881—882).—If anaërobic conditions are observed, cod-liver oil can be hardened at a temperature of 150° and deodorised without any appreciable loss in the vitamin-*A* content. S. S. Z.

Investigation of Barley, Malt, and Beer for Vitamins-*B* and -*C*. A. HARDEN and S. S. ZILVA (*Biochem. J.*, 1924, **18**, 1129—1132).—The vitamin-*B* of barley is not affected by the malting process and is frequently present in the finished malt, but is absent from the culms. The antiscorbutic vitamin appears in the steeped grain and is present in the green malt but absent from kilned malt. The beer examined by the authors (India Pale Ale) was free from both vitamins-*B* and -*C*. S. S. Z.

Fractionation of Bios and Comparison of Bios with Vitamins-*B* and -*C*. G. H. W. LUCAS (*J. Physical Chem.*, 1924, **28**, 1180—1200).—The bios contained in malt combings and in rice-polishings can be fractionated by precipitation in alcoholic solution with barium hydroxide into bios I and II, neither of which has by itself any great influence on the rate of reproduction of *Saccharomyces cerevisiæ*, race F, but together enormously increase the crop of yeast. A top yeast is described, however, which is much less dependent on bios than race F. Bios I and II cannot replace the vitamins in preventing polyneuritis in pigeons or scurvy in guinea-pigs or in maintaining the growth of rats. The growth-producing vitamin can be extracted from rice-polishings by treatment with pepsin. The chemical treatment employed in the fractionation of bios destroys the growth-promoting vitamin. M. B. D.

Action of Nitrous Acid on the Antineuritic Substance in Yeast. R. A. PETERS (*Biochem. J.*, 1924, **18**, 858—865).—Primary and many secondary amines are not responsible for the antineuritic activity of acid extracts of yeasts, since such extracts retain their activity after being treated with nitrites. Histamine sometimes cures polyneuritis in pigeons; this confirms Abderhalden's observations. Daily doses of this drug do not, however, delay the onset of the disease. S. S. Z.

Dietetic Value of Barley, Malt, and Malted Liquors as Determined by their Vitamin Content. H. W. SOUTHGATE (*Biochem. J.*, 1924, **18**, 769—776).—Barley and malt, tested on rats, have been found to contain water-soluble-*B* in considerable and equal amounts. Malt has also been shown to possess antineuritic properties in the case of pigeons fed on a basal diet free from vitamin-*B*. Beer independent of its yeast content contains vitamin-*B*, but to a much less extent than that the corresponding amount of malt used in its manufacture. Vitamins-*A* and -*C* are not present in appreciable quantities in barley or its derivatives. S. S. Z.

Nutritive Properties of Milk. III. Effectiveness of the *X*-Substance in Preventing Sterility in Rats on Milk Rations High in Fat. H. A. MATTILL, J. S. CARMAN, and M. M. CLAYTON (*J. Biol. Chem.*, 1924, **61**, 729—740).—Rats of both sexes fail to reproduce on a milk diet of high fat content; the addition of nucleoprotein to such a diet has no effect, but reproductive power is retained if wheat embryo in added to the food; preliminary ethereal extraction of the wheat embryo, however, deprives the latter of its curative power. This observation, together with the fact that addition of green lettuce leaves to the diet will also prevent sterility, indicates that the missing factor is the substance designated "*X*" by Evans (*J. Metabol. Res.*, 1923, **3**, 233). C. R. H.

Extraction and Determination of Lipochromes from Animal and Plant Tissues. K. H. COWARD (*Biochem. J.*, 1924, **18**, 1114—1122).—The only quantitative method of extraction is saponification in an atmosphere of nitrogen with aqueous potassium hydroxide of not higher strength than 20%. Cvet's observation on the existence of four xanthophylls has been confirmed by employing his chromatographic method (fractional filtration of the pigments through a column of chalk). This method has also been found suitable for separating carotin and lycopin from a mixture of the two pigments. A curve for use with the Hellige colorimeter is given for the determination of carotin. S. S. Z.

Lipochromes of Etiolated Wheat Seedlings. K. H. COWARD (*Biochem. J.*, 1924, **18**, 1123—1126).—The pigments of etiolated wheat seedlings are carotin and the four xanthophylls isolated by Cvet from green leaves. It is impossible to obtain quantitative figures for the four xanthophylls by Cvet's chromatographic method. S. S. Z.

Yellow Pigments of Australian Acacias. J. M. PETRIE (*Biochem. J.*, 1924, **18**, 957—964).—The water-soluble yellow pigment of *Acacia linifolia*, *A. decurrens*, and *A. longifolia* is a glucoside which on hydrolysis yields flavonol, kaempferol, and rhamnose. Free flavonol is absent. The yellow flavonol obtained on hydrolysis can be transformed by reduction with nascent hydrogen into a red solution resembling that of anthocyanins. The acacia tannins are composed of phloroglucinol and protocatechuic and gallic acids, and deposit on hydrolysis large amounts of the red phlobaphen anhydrides. The flavonol is present in quantities of about 0·06% of the fresh flower, carotin and xanthophyll from 0·14 to 0·3%. S. S. Z.

Grape Pigments. III. Anthocyans of Seibel Grapes. R. J. ANDERSON (*J. Biol. Chem.*, 1924, **61**, 685—694; cf. this vol., i, 1152).—The pigment occurring in the skins of the hybrid Seibel grapes was isolated as the *picrate*, red needles, and converted into the *chloride*, $C_{23}H_{25}O_{12}Cl$, prisms ($+3H_2O$), m. p. 160° (sintering at 158°); on hydrolysis with hydrochloric acid this yields the *anthocyanidin chloride*, $C_{17}H_{15}O_7Cl$, prisms ($+1{\cdot}5H_2O$), m. p. above 260° [*picrate* ($+H_2O$)]. Glucosazone was isolated from the filtrate after the hydrolysis. Methoxyl determinations indicated that the anthocyanidin was a mixture of the mono- and di-methyl ethers of delphinidin, containing a preponderance of the dimethyl ether. Delphinidin iodide was isolated from the solution after removal of the methoxyl groups. Details are given of the absorption spectra of the chlorides of the anthocyanin and anthocyanidin. C. R. H.

Sitosterol. R. J. ANDERSON and F. P. NABENHAUER (*J. Amer. Chem. Soc.*, 1924, **46**, 2113—2118).—A sample of sitosterol obtained from the bottom fraction of maize-gluten sterols as previously described (this vol., i, 924) was acetylated and brominated by Windaus and Hauth's method (A., 1907, i, 921). On debromination with zinc dust and acetic acid in alcoholic solution followed by hydrolysis with alcoholic potassium hydroxide, a sitosterol was obtained which on recrystallisation had m. p. 138—139°, $[\alpha]_D^{20}$ —36·69°; acetyl derivative, m. p. 130—131°, $[\alpha]_D^{20}$ —40·20°. Sitosterol from wheat bran and from crude maize oil similarly purified yielded products having m. p. 140—141°, $[\alpha]_D^{20}$ —34·90° (acetyl derivative, m. p. 130—131°), and m. p. 138—139°, $[\alpha]_D^{20}$ —34·87° (acetyl derivative, m. p. 128—130°, $[\alpha]_D^{20}$ —38·81°), respectively, and it is concluded that sitosterol as usually prepared is contaminated with small amounts of dihydrositosterol. The approximate composition of a mixture of the two sterols can be calculated from the formulæ $S=(25{\cdot}82-R)/0{\cdot}6246$ and $P=(36{\cdot}64+R)/0{\cdot}6246$, where S and P represent the percentages of sitosterol and dihydrositosterol respectively, and R is the specific rotation of the mixture in chloroform, the values —36·64° and +25·82° being chosen for the specific rotations of the respective pure sterols. R. B.

Non-volatile Acids of the Peach. E. K. NELSON (*J. Amer. Chem. Soc.*, 1924, **46**, 2337—2338).—Fractionation by the ester-hydrazide method shows that the non-volatile acids of the peach consist chiefly of *l*-malic acid and citric acid in approximately equal proportions. The m. p. 145° is recorded for citric acid trihydrazide (cf. Curtius, A., 1917, i, 635; Franzen and Helwert, A., 1923, i, 637). R. B.

Non-volatile Acids of the Dried Apricot. E. K. NELSON (*J. Amer. Chem. Soc.*, 1924, **46**, 2506—2507; cf. preceding abstract). —The non-volatile acids of the dried apricot, identified by esterification, fractionation, and conversion into the hydrazides, consist of *l*-malic and citric acids in the proportion 2·5 : 1, with traces of an unidentified acid, possibly oxalic acid. F. G. W.

Acetaldehyde: A Normal Constituent of the Tannin-rich Contents of the "Inclusion" Cells in the Mesocarp of certain Fruits. C. GRIEBEL (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 218—220).—In a previous paper (this vol., ii, 791) the presence of small amounts of acetaldehyde was demonstrated in certain fruits. The so-called inclusion cells (A., 1919, i, 427) were found to contain acetaldehyde readily liberated from the cell by distillation with 2% tartaric acid. The contents of the inclusion cell of *Ceratonia siliqua*, L, separated by mechanical means, gave a considerable amount of acetaldehyde on distillation with water alone, a further yield being obtained by distillation with acid. The acetaldehyde is considered to be responsible for the coagulation and consequent disappearance of the rough taste of the tannins during the process of ripening. G. S. W.

Ripening Process of Bananas. C. GRIEBEL (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 211—227).—During the ripening of bananas the tannin-rich cell contents of the latex tubes present in the pith become coagulated and the tannins pass from a soluble to an insoluble condition. Subsequently the latex tubes break down forming the so-called inclusion cells. These cells are found to contain acetaldehyde in an easily liberated condition (cf. preceding abstract). Fruit in which the normal process of ripening has been suppressed by frost is tasteless and odourless, the formation of sugar from starch and the production of amyl acetate having been inhibited; at the same time, the fruit contains tannin in a soluble condition and only traces of acetaldehyde are present. G. S. W.

Wax from *Fagrœa*. A. J. ULTÉE (*Bull. Jard. Botan. Buitenzorg*, 1924, **6**, [3], 1—3; from *Chem. Zentr.*, 1924, i, 2882).—The fruits of *Fagrœa* have beneath the outer integument a layer of white, glutinous substance from which, by coagulation with alcohol, a white, slightly elastic mass was obtained, containing ash 0·23%, protein 0·22%, caoutchouc 5·16%. From the first alcoholic extract crystals, m. p. 79°, were obtained which yielded on hydrolysis lupeol, m. p. 211°, and palmitic acid. Phytosterol was also present. G. W. R.

Isolation of an Inhibitory Substance from Plants. W. L. MALLMANN and C. HEMSTREET (*J. Agric. Res.*, 1924, **28**, 599—602). —A substance which inhibits the activity of the cabbage-rot organism was isolated from rotted cabbage plants. The substance was effective against other "soft-rot" organisms, and gave positive results at exceptionally great dilution. It was destroyed by exposure to a temperature of 63° for 30 minutes, but survived after 20 minutes at 56°. It is not considered to be a product of the soft-rot organism. A. G. P.

Action of Bromine on certain Plants. A. Pitini (*Arch. Farm. sperim. aff.*, 1924, **38**, 164—168).—Decomposition of glucosides contained in plants by the action of bromine (cf. Liotta, A., 1920, i, 587) is the result of a hydrolytic process and takes place either not at all or only partly if the plants are first thoroughly dried. Alkaloids contained in plants are unaffected by bromine only if they are stable towards the halogen hydracid which is formed. T. H. P.

Absorption of Carbon Dioxide the First Step in Photosynthesis. H. A. Spoehr and J. M. McGee (*Science*, 1924, **59**, 513—514).—Dried and ground leaf material, to which the same amount of water has been added as was originally contained in the leaves, absorbs carbon dioxide from the air in the dark; the manner of drying the leaves, however, greatly affects their absorptive capacity. *Helianthus* leaves, similarly treated and free from carbon dioxide, absorbed 4·59 mg. of the latter per g. at 25°. Extraction of the dried leaves with cold absolute alcohol greatly, and with water somewhat, reduced the absorptive capacity, but the material extracted by the alcohol absorbed only very small amounts of carbon dioxide. The absorptive capacity of the leaf is also destroyed by heat. Extraction with acetone did not affect the absorptive capacity, but the latter was reduced by 90% by extraction with water saturated with ether at 20° (Chibnall and Schryver's method for protein extraction), the residue absorbing as much carbon dioxide as the original leaf material. It is considered that support is accorded to the theory that the leaf absorbs carbon dioxide from the atmosphere by a mechanism similar to that which in the blood of mammals serves to free the tissues from this gas. The major portion of the carbon dioxide is probably absorbed by the proteins of the leaf; this primary union may be of importance in determining the cause of the asymmetric nature of the synthesis of carbohydrates in the chlorophyllous plant. A. A. E.

Water Content, a Factor in Photosynthesis. R. H. Dastur (*Ann. Bot.*, 1924, **38**, 779—788).—Inadequate water-supply results in a decline in the photosynthetic activity of leaves and ultimately causes their decay. This factor also accounts for the fact that Willstätter and Stoll were unable to obtain constant values for the assimilation numbers of the leaves of the same species. O. O.

Chemonastia of *Drosera rotundifolia*. I. W. Mevius (*Biochem. Z.*, 1924, **148**, 548—565).—Solutions of the sodium halides cause inflection of the leaf tentacles of *Drosera rotundifolia*, the duration of which varies with the concentration of the stimulating solution, whilst weak solutions produce a quicker response than concentrated solutions. Sodium nitrate is a more active stimulant, but is also more injurious to the leaves than the halides, whilst sodium sulphate only excites the tentacles in concentrated solutions. Potassium salts show somewhat parallel results, but here the more concentrated solutions act more quickly. The activity of the anions follows the series: $NO_3 > I > Br > Cl > SO_4$. The alkaline-earth chlorides warmed at 51° inhibit the inflection of the tentacles, a similar result being obtained with warm 0·25*N*-potassium chloride solution. A chemical stimulus and a heat stimulus do not summate. *Drosera* leaves kept in a strong solution of alkaline-earth salt and then placed in sodium chloride show an immediate infolding of the tentacles. The alkaline-earth salts exert no harmful action on the leaves. J. P.

Nitrate-reducing Properties of Plants. V. L. ANDERSON (*Ann. Bot.*, 1924, **38**, 699—706).—Nitrate is frequently found in green plants. Of the plants examined more than 20% contained nitrite. The nitrate-reducing mechanism "atite" (cf. Haas and Hill, this vol., i, 349) was observed in 23 plants. Atite does not appear to be of much significance in the protein metabolism of the plant. O. O.

Influence of Nitrifying Bacteria on the Growth of Barley. E. B. FRED (*Soil Sci.*, 1924, **18**, 323—329).—The yield of barley (total dry weight), grown under sterile conditions in sand supplied with nutrient salts and nitrogen as ammonium sulphate, was nearly doubled when pure cultures of nitrifying bacteria were added 2 weeks before planting. The favourable effect on the plants was evident throughout growth, and the presence of nitrates in the inoculated pots and their absence from the others was confirmed by test. The barley contained 0·78% of nitrogen when nitrifying organisms were present and 0·66% in their absence. C. T. G.

Relation of the Molecular Proportions in the Nutrient Solution to the Growth of Wheat. M. C. SEWELL (*J. Agric. Res.*, 1924, **28**, 387—393).—Wheat plants were grown in sand cultures with nutrient solutions containing varying proportions of dissolved salts. Grain yields were as good from solutions high in nitrogen and low in potassium and phosphate as from those with less nitrogen but higher proportions of phosphate and potassium salts. A. G. P.

Antagonism of Hydrogen Ions and Neutral Salt Ions in their Action on the Germination and Growth of Wheat. H. LUNDEGÅRDH (*Biochem. Z.*, 1924, **149**, 207—215).—Calcium and potassium chlorides and sodium dihydrogen phosphate diminish the toxic effect of increasing hydrogen-ion concentrations on the growth of wheat seedlings, more especially between p_H 4·5 and 6·8. The antagonism between salt and hydrogen ions is also shown in their action on germinating wheat seeds. J. P.

Nitrogenous Constituents of the Juice of the Alfalfa Plant [Lucerne]. II. Basic Nitrogen. H. B. VICKERY (*J. Biol. Chem.*, 1924, **61**, 117—127; cf. this vol., i, 1275).—In addition to the asparagine and tyrosine already reported, there have been isolated, from the unhydrolysed juice of the lucerne plant, arginine, lysine, stachydrine, choline, a purine in the form of its chloride, and a base (unidentified) which gives a picrate melting at 298°. Taken together, the substances so far isolated account for 4·8% of the organic solids and 13·6% of the total nitrogen of the protein-free solution obtained by treating the original juice with alcohol. C. R. H.

Variation with Temperature of the "Swelling Value" of Amylogen. A. Maige (*Compt. rend. Soc. Biol.*, 1924, **90**, 685—687; from *Chem. Zentr.*, 1924, i, 2784—2785).—In experiments with the embryos of germinating beans, the critical concentration of sugar at which starch is transformed into amyloplasts was found to be increased both by raising and by lowering the temperature. G. W. R.

Methylpentosans in Cereals. G. Testoni.—(See ii, 790.)

Determination of Nitrate and Ammonia in Nitrogenous Materials. O. M. Shedd (*J. Agric. Res.*, 1924, **28**, 527—539).—The Devarda alloy method of Strowd (*Soil Sci.*, 1920, **10**, 333) is modified by allowing the reduction to take place at ordinary temperatures for 24 hours previous to heating. A control experiment on a portion of the test-liquid without Devarda's alloy is carried out with each determination. The method was used for determining nitrate in tobacco leaves and is suitable for the examination of fertilisers. Where nitrate and ammonia are to be determined in portions of the same solution a preliminary filtration is advised. A. G. P.

Determination of Ammonia in Soil. N. Bengtsson (*Soil Sci.*, 1924, **18**, 255—278).—By successive extractions of soil with potassium chloride solution (25 g. of soil extracted with, at the most, seven 100 c.c. portions of approximately 4% solution), added ammonia could be recovered quantitatively and determined in the combined filtrates. Very low figures were obtained by this method for the ammonia present in air-dried arable soils, indicating that organic nitrogen compounds are not decomposed. A detailed procedure is given (cf. *B.*, 1924, Dec. 26) which proved entirely satisfactory with all surface soils, but failed in the case of one heavy clay subsoil. C. T. G.

Methods of Studying the Strength of Soil Acids. J. W. Tidmore and F. W. Parker (*Soil Sci.*, 1924, **18**, 331—338).—A comparison of the strength (intensity factor) of the soil acids in 25 soils, as determined by the Truog "avidity" method (cf. A., 1916, ii, 404), by the sugar inversion method (cf. Rice and Osugi, A., 1918, i, 520), and by the hydrogen-ion concentration showed good correlation between the results. The methods are based on different principles, and the close agreement between the results obtained may be explained by assuming that the acids of the solid phase undergo hydrolysis producing hydrogen ions, the extent of such hydrolysis depending on the strength of the acids. It is considered that the results support the view that the p_H of the soil solution is largely determined by the acid silicates of the soil. [Cf. *B.*, 1924, Dec. 26.] C. T. G.

Influence of Sulphur Oxidation on Solubility of Soil Minerals. R. E. STEPHENSON and W. L. POWERS (*Soil Sci.*, 1924, **18**, 317—321).—The application of various amounts of sulphur to soil maintained at optimum moisture content greatly increased the water-soluble calcium and potassium and decreased the water-soluble phosphorus. Nitrification was depressed by the heaviest application and there was an appreciable increase in acidity. Two soils were used, one representative of arid conditions, with p_H 7·0, and the other of humid conditions, with p_H 6·4. Flocculation of the colloidal material of the soils by the products of oxidation of the sulphur was very marked. It is suggested that the increase in the soluble calcium may account to some extent for the response given by leguminous crops, especially lucerne, to light dressings of sulphur on certain soils. C. T. G.

Absorption of Bases by Soils. N. M. COMBER and S. J. SAINT (*Soil Sci.*, 1924, **18**, 131—132).—Jones (this vol., i, 820) claims to have shown that beyond a certain point an increase in concentration of a base in solution results in a decrease in the amount absorbed by a soil in contact with the solution. This conclusion is based on determinations of the carbon dioxide evolved on shaking carbonates and hydrogen carbonates of alkali and alkaline-earth metals with soil. In the experiments with normal carbonates, the carbon dioxide given off will form hydrogen carbonate with the remaining carbonate and hence cannot be taken as a measure of the amount of base absorbed. Experiments in which the amount of base absorbed by a soil is calculated both from the carbon dioxide evolved and by titration after filtering show definitely that Jones' conclusions are not justified. C. T. G.

Resistance of Soils to Acidification. A. DEMOLON and V. DUPONT (*Compt. rend.*, 1924, **179**, 300—302).—Aqueous extracts of soils from various sources, from which calcium carbonate has been excluded, behave towards both sulphuric and lactic acids as weak buffer solutions. This property is attributed to the humates present. When the soil remains in contact with the aqueous extract, the colloidal clay reacts with sulphuric acid so that the suspension exhibits marked buffer action. H. J. E.

Microscopical Study of Soil. S. WINOGRADSKY (*Compt. rend.*, 1924, **179**, 367—371).—A method of soil treatment is described which yields five specimens for examination from each sample. These are stained with erythrosin. From observation of a series of such specimens the following general conclusions are drawn. Normal arable soil contains only cocci in groups; these are surrounded by a gel or membrane and firmly attached to the particles resulting from flocculation of colloid matter. Mineral débris, except in so far as it is colloidal, is free from microbes; this applies particularly to the coarser particles. In the case of soils to which soluble fermentable matter has recently been added, free microbes, distributed in irregular clusters, predominate. These often consist of forms which are not present in normal soil and are not associated with colloidal particles. A soil which is foul may readily be recognised by the bacterial forms present in the solution even after centrifuging. [Cf. *B.*, 1924, Dec. 26.] H. J. E.

Secular and Seasonal Changes in the Soil Solution. J. S. Burd and J. C. Martin (*Soil Sci.*, 1924, **18**, 151—167).—The concentration and composition of the soil solutions, obtained by the displacement method, from seven soils have been compared, portions of each soil having been kept for 8 years under different conditions, namely, cropped, fallowed, and air-dried. The displaced solution is taken as a trustworthy measure of the true soil solution (cf. *J. Agric. Sci.*, 1923, **13**, 265) and it is assumed that the air-dried soils have remained unchanged and represent the condition of the soils at the beginning of the 8-year period. The cropped soils all showed a marked decrease in concentration of total solutes and nitrates in the displaced solutions at the end of the period, whilst the fallowed soils, with one exception (a highly productive soil), gave considerably increased concentrations. The concentration of phosphate in the cropped soils is decreased—an unexpected result, since it is known that phosphate tends to form a saturated solution and re-establish equilibrium very rapidly. The concentration of sulphate increased in both cropped and fallowed soils.

With soils in a low state of fertility due to continuous cropping, there is a seasonal decrease in concentration of most of the solutes, but the initial concentration of the soil solution in any given growing season returns to its original magnitude by the beginning of the following season. The results cannot be taken to apply to natural drained soils in which the effect of leaching comes into play, since the experimental soils were kept in vessels allowing no escape of drainage water. C. T. G.